

Topical Report

May 17, 2001

Surface Acoustic Wave Mercury Vapor Sensor

Work Performed Under Contract:

DE-AR26-97FT34316

Submitted By:

**Sensor Research and Development Corporation
17 Godfrey Road
Orono, Maine 04473**

Principal Investigator: Dr. George P. Miller

Phone Number: 207-866-0100

Fax Number: 207/866-2055

Submitted To:

**U. S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia
COR: James Huemrich**

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

Sensor Research and Development Corporation (SRD) has been contracted to develop and deliver a prototype instrument capable of the detection and measurement of low levels of gaseous mercury for use in thermal waste treatment continuous emissions monitoring. The goal is to develop a fast, simple, inexpensive and reliable sensor-based instrument for detecting and monitoring vaporized mercury that should be able to react to low (less than 5 $\mu\text{g/dscm}$) levels of mercury vapor, be site deployable, and provide continuous data on cumulative mercury exposure and instantaneous concentration.

In order to develop the necessary knowledge base, which would enable a commercially viable SAW based mercury vapor sensor, several important technical objectives had to be accomplished in two distinct phases. The first phase of the project included (i) the development of a heater element to optimize the sorption and desorption of mercury vapor on the gold sensing film, (ii) the determination of the optimum gold film thickness and operating temperature for the sensing element, (iii) the characterization of the SAW sensor response signature, and (iv) the determination of the sensor selectivity. The second phase included (i) the detailed definition of the thermal waste treatment application and environment to which the prototype was designed, (ii) the fabrication of a field deployable prototype instrument, (iii) extensive laboratory testing of the sensor instrument, and (iv) field testing and demonstration of the sensor instrument. During the base phase of the contract, gas delivery systems for mercury and mercuric chloride were designed and constructed, optimal sensing film parameters (including film thickness, operating temperature, and adhesion layer) were experimentally selected, and a sensing element was designed and constructed based on these parameters. Testing of the sensing element was performed. Testing included measurements of responses to mercury and mercuric chloride at concentration ranges from less than 0.1 $\mu\text{g/dscm}$ to 120 $\mu\text{g/dscm}$, and measurements of responses to these gases in the presence of NO_x , SO_x and high humidity. Other efforts during the base phase focused on completing the base contract and planning for the work to be performed under Option 1.

Under the Option phase of the contract, exercised by the Department of Energy (DOE) in mid 1999, SRD took the basic sensor design and began the process to integrate the technology into a prototype Continuous Emission Monitor (CEM). Specifically, SRD constructed a breadboard prototype, and two prototype sensors during the option phase of the contract. The breadboard and prototype systems were used to test whether the basic sensor technology and software algorithms was sufficient to meet the requirements necessary in a commercial CEM. Components of the breadboard system were integrated into prototype 1, which was constructed for elemental Hg testing and software development. Instrument 2 included a heated gas path and electronics improvements developed during testing using instrument 1. Integrated testing was performed at the University of North Dakota, Energy and Environmental Research Center (EERC) in March, 1999. The Option phase of the contract was further modified in mid 2000 and the decision made by DOE was made to integrate SRD's sensor with a gas sampling and preconditioner to be provided by DOE. This decision, allowed SRD to focus on the sensor requirements of a CEM leaving the sampling and speciation requirements to be met by the system to be provided by DOE. The sensor system was modified to increase sensitivity, allow continuous operation, and provide the potential to handle large mercury spikes. This recent work, including the results of the latest Field Test, is presented in this topical report.

Table of Contents

Abstract	iii
Need Statement	5
Significance of the Problem	5
Importance of the Work.....	6
Merit of the Technology	7
Performance Improvement and Cost Savings	7
Applicability to DOE Sites.....	8
Prior Uses of Proposed Technology.....	9
Commercial Potential of the Proposed Technology	9
Company Description	9
Competitive Products	10
Commercialization.....	10
The Study	11
Description of the Technology	11
Operating Temperature.....	13
Speciation.....	15
Interference Effects.....	15
Film Thickness.....	17
Present Status	18
Sampling System:	19
Spike Testing	22
Continuous Tests	25
UND-EERC Field Test.....	25
Hg North Dakota University EERC Test Plan – March 2001	25
Tuesday March 13th.....	25
UNDEERC Testing Facility.....	26
Spike Test Results:	27
Continuous Test Results:	31
Conclusions and Recommendations	35
Publications, Patents, and Theses.....	36
References	36
List of Acronyms and Abbreviations	38

Need Statement

Significance of the Problem

Fossil fuel combustion is the largest contributor of atmospheric emissions. In November, 1999, the Coal-Train Coalition reported that each year some 400 coal burning power plants in 43 states are emitting an estimated 98,000 pounds of mercury into the air. However, a potentially large contributor could come from the remediation of DOE's mixed low level wastes (MLLW) whether this remediation is performed by thermal or non-thermal treatment systems. Of all the trace metals contained in these emissions, mercury is the greatest concern since it is the most volatile of the metals, is widespread, highly mobile, very toxic, and has long-term persistence in the environment.¹ Mercury is particularly dangerous since it can bio-accumulate within the food chain and lead to irreversible neurological disorders and other health related problems. A recent biological and environmental study throughout the State of Maine, for example, has shown that mercury is concentrated from low levels (~1 ppb) in ponds to levels as high as 40 ppm at the top of the food chain (in bald eagles). These levels can have serious implications for people who regularly eat fish, which exhibit mercury levels of approximately 2 ppm. The accumulation of mercury in the ocean has even more serious implications, since a large portion of the world's food supply is obtained from marine sources. Furthermore, the accumulation of more than 2 ng/ml of mercury in drinking water exceeds levels dictated by the Safe Drinking Water Act and poses an immediate threat to health.

Mercury is the major contaminant of the volumes of hazardous wastes (containing organic and/or toxic metals) and mixed wastes (containing combined hazardous and radioactive chemicals) generated by the US Department of Energy (DOE) weapons production complex. High-level and low-level mixed waste streams have been stored in tanks or burial grounds while other hazardous waste streams were routinely disposed to the ground surface, ponds, trenches, and other liquid discharge facilities. Leaks from tanks and process piping, leachate from burial grounds or storage areas, and liquid discharges to the soil have resulted in widespread contamination of soils and groundwater at many DOE sites.

At the Federal, State, and local levels, laws and regulations exist for the remediation and restoration of contaminated sites, elimination of pollutants and the strict management of necessary emissions. Regulatory limits for mercury emissions from thermal and non-thermal treatment units are becoming increasingly stringent. Under the MACT rules, there is a corresponding goal to deliver technologies that can make these operations more efficient and less costly, enhance meeting permit requirements, and satisfy processing monitoring needs. Development of cost-effective innovative technologies for the characterization and monitoring of hazardous waste sites and for the real-time process control of waste treatment operations is not only a requirement for DOE, but also for other Federal agencies, State agencies and commercial businesses.

The requirement for remediation and prevention is broad based and includes Federal, State and local government agencies, the Department of Defense, and much of industry. The magnitude of the problem is clearly indicated by noting that DOE alone is responsible for waste management and cleanup of more than 100 contaminated installations in 36 states and territories. Additionally, there are approximately, 5,000 peripheral DOE properties (e.g., residences and businesses) that have soil contaminated with heavy metals. DOE has identified more than 1.5

million 55-gallon drums and boxes of waste in storage, 3 million cubic meters of buried waste, and 77 million gallons of high-level waste contained in 332 underground storage tanks.

In addition to DOE, both the Department of Defense (DOD) and the Environmental Protection Agency (EPA) are actively involved in mercury cleanup and remediation. EPA has identified over 1,200 additional sites with sufficient contamination to place them on their National Priorities List (NPL). DOD is responsible for the cleanup of their facilities contaminated as a result of training, industrial, or research activities and has identified approximately 7,000 sites world-wide that will require remediation. In 1997, an EPA/DOE-sponsored demonstration of the available multi-metal continuous emission monitors was conducted. Of the technologies tested, the inductively coupled plasma-based instruments were the most promising, however, none received a passing grade. As recently as December 14, 2000, the EPA issued a decision to regulate mercury emissions from power plants by 2004. In support of this requirement, the EPA conducted an ETV Advanced Monitoring Systems Hg CEM Verification Phase I test, Jan 15-26, 2001 of the commercially available technology.

DOE's recent decision to move towards the alternative treatment of waste does not negate the need for mercury CEMs emissions from treatment methods such as plasma torch and induction furnaces, and they will still require monitoring. The technology underlying the commercial instruments being evaluated is either based on atomic absorption, atomic fluorescence or atomic emission.² These are mature technologies and their inherent technical limitations are such that as the industrial release of mercury into the environment is further restricted or reduced, other techniques will be required to monitor both its emission and distribution.

Importance of the Work

In order to achieve the government-set remediation and restoration goals, advanced sensor-based instrumentation with improved selectivity, longevity and sensitivity are needed to provide real-time process control of waste treatment incineration processes, as well as meet the characterization and monitoring requirements of waste sites. Verification and monitoring technologies are needed to ensure worker safety and effective cleanup during remediation, treatment, and site closure activities. Specifically, technologies are sought for the development of sensors and instrumentation for the measurement of the chemical properties of hazardous wastes; for the nondestructive assay of chemical contaminants in process equipment, ducts, and pipes; and for monitoring barrier emplacement and performance. Measurements are needed to determine properties such as chemical speciation, gas generation rates and types, and real-time, head-space gas build-up. Continuous emission monitoring in off-gas systems for thermal and non-thermal processes will be critical in ensuring the success of new treatment technologies. Monitoring of heavy metals emissions is a crucial need that will facilitate the permitting and public acceptance of these treatment processes.

Current effluent measurement techniques are based on extractive samples followed by chemical analysis (e.g. EPA Reference Method 29 or Ontario Hydro method). In addition to being expensive and subject to human error, these methods provide no real-time data for operational feedback. Results can take two to four weeks from the time of sampling. A critical need exists for a fast, simple, inexpensive, and reliable sensor instrument for detecting and monitoring vaporized mercury. Such a sensor should be able to react to extremely low (<8 µg/dscm) levels of mercury vapor, should be field deployable, and provide continuous data on either cumulative mercury exposure or instantaneous concentration. Mercury emissions

monitoring from thermal and non-thermal treatment processes associated with remediation efforts will be required to demonstrate the effectiveness of mercury control methods and to provide the real-time process control of the system. Monitoring of mercury off-gas emissions is a crucial need that will facilitate the licensing and permitting of mixed waste treatment systems, as well as a potential upgrade to industrial waste treatment facilities worldwide. In addition, this technology has the potential to meet the environmental monitoring needs of the coal combustion industry.

Merit of the Technology

Performance Improvement and Cost Savings

The technology embodied in the proposed SAW mercury vapor sensor has features and properties that offer important advantages in the following areas:

- Cost - projected to have a substantial net cost advantage over competing technologies. (Estimated at less than \$2,000/ unit in production).
- Reliability - predictable, repeatable performance with little or no maintenance requirements when deployed.
- Sensitivity - highly sensitive to mercury vapor over a broad range of concentrations (Estimated dynamic range from less than 0.1 $\mu\text{g/dscm}$ to greater than 20 $\mu\text{g/dscm}$ continuous, ~ 1000 $\mu\text{g/dscm}$ spike).
- Operational utility - simple, rugged modular design with low power requirement and portability.
- Flexible implementation - adaptable as either CEM, process control instrument, fixed remote site monitor, or portable site characterization instrument.
- Safe and nonpolluting.

A number of review articles are available which describe the current technology available for the detection of gaseous mercury.^{1,2} Briefly, these techniques fall into four basic categories: wet chemistry (e.g. EPA RM 29), optical techniques, chemiresistive sensors, and acoustic microbalances.

Chemiresistive sensors, such as that proposed by McNerney etc. al.³ and subsequently commercialized by Jerome Instruments,⁴ are based upon conductivity changes manifested in a metal film upon amalgamation of mercury. These sensors are small, fast, capable of *in situ* operation and relatively inexpensive. Because of the extremely thin metal films required for reasonable sensitivity, however, this particular class of mercury sensors has a very limited dynamic range, saturating very quickly and subject to contamination.

Optical techniques are also available for the selective detection of mercury, as well as other heavy metals. An EPA sponsored test of the available commercial mercury CEMs is presently underway at EPA RTP RKIS facility in North Carolina. involving a number of the following technologies. Several well-known technologies, such as Cold-Vapor Atomic Absorption (CVAA), and Cold-Vapor Atomic Fluorescence (AF) require wet chemistry, preconcentration and/or the use of a non-quenching atmosphere.⁵ Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) has promise but for air operation the detection limit is limited to above 5 $\mu\text{g/dscm}$.⁶⁻⁹ The use of argon-based plasma and a vacuum-UV spectrometer improves the detection but at substantially increased complexity and cost.¹⁰ Laser-Induced

Breakdown Spectroscopy (LIBS)¹¹ while touted as an *in situ* technique suffers in sensitivity due to the presence of mercury self-absorption and has calibration difficulties. Cavity ringdown spectroscopy has potential as an ultra-trace technique for mercury, but at this time, requires expensive equipment.^{12,13}

The final category is the area of the acoustic microbalance. Bristow,¹⁴ and later, other investigators¹⁵⁻²¹ demonstrated that a gold-coated quartz crystal microbalance (QCM) could detect mercury. The instrument had several key advantages over other technologies; it was cheap, reliable, fast, selective, small and rugged. The major drawback of the QCM technology however, is its relatively low sensitivity.

The proposed technology for a SAW mercury sensor falls into the category of acoustic microbalances. SAW devices, however, are capable of operating at frequencies hundreds of times higher than those possible with QCMs. Because mass sensitivity increases exponentially with frequency, this technology combines all of the benefits of the QCM with the extremely high sensitivities previously achievable only with optical and mass spectroscopy instruments. A final commercial instrument or CEM is expected to cost less than \$2000 and fit in a space smaller than a deck of playing cards. The complete sensing element itself, including the SAW resonator and heater/cooler, in fact, is smaller than a pencil eraser and costs less than \$50. The remaining electronics can be situated several feet away as one component of a larger multi-gas/multi-sensor array, as a process control instrument, or in any other configuration dictated by a specific application. Operating costs for the instrument are expected to be less than \$50 per month. Other advantages of the proposed instrument over many currently available instruments are higher reliability (no moving parts), the lack of any polluting byproducts, and a mature underlying technology (SAW resonators have been used for several decades in signal processing, frequency control and sensing applications).

Applicability to DOE Sites

SRD Corporation expects that the results of the basic SAW/thin film research obtained in this project will demonstrate an innovative microsensor technology, which will result in a new generation of highly sensitive, highly selective, low cost portable sensors. These sensors have the potential for numerous applications within the Department of Energy and its related activities.

The initial application, and subject of this report, is a mercury vapor sensor configured as a prototype process control instrument for thermal and/or non-thermal waste treatment facilities. The simplicity, sensitivity, and reliability enable the proposed sensor to monitor mercury vapor at concentrations substantially below regulated levels in real-time and at very low cost.

The same instrumentation is readily adaptable for the monitoring of mercury vapor emissions from fossil fuel combustion processes and as a remote/portable (ambient air) monitor for characterization and post-remediation monitoring of hazardous waste sites.

The sensor technology being developed for the detection of mercury vapor is potentially extendible to aqueous mercury through the integration of a fluid collection and vaporization chamber. This sensor would find significant application within the DOE Decontamination and Decommissioning (D&D) effort since former nuclear weapons manufacturing sites are heavily polluted with mercury as well as radionuclei (uranium and plutonium) and in those states, like Maine, with documented mercury-contaminated water problems.

Outside of governmental requirements, there is a significant application of an aqueous sensor is for drinking water sensors. These would be configured as instruments to field test new or existing wells, continuously monitor water in the home or fixed monitor systems for municipal water supplies.

Prior Uses of Proposed Technology

Since the advent of practical surface acoustic wave generation techniques²² over three decades ago, SAW technology has been used in numerous frequency control and signal processing applications. SAW resonators are found today in almost every personal computer, garage door opener, and cellular telephone on the market; and SAW filters are also found in applications ranging from chirped RADAR to GPS. The use of SAW devices in sensing applications first surfaced in 1975 when Reeder et. al.²³ used a SAW oscillator to measure pressure. Similar sensors soon followed for measuring temperature,^{24,25} voltage²⁶⁻³⁴ and polymer phase transitions.³⁵⁻⁴⁰ In 1979, Wholtjen and Dessy first suggested the use of SAW devices as gas sensors. Since this initial suggestion, SAW devices have been used to sense gases such as SO₂, H₂S, NO, NO₂, CO, CO₂, CH₄, CH₃SH, etc. Arrays of SAW sensors, coupled with artificial neural networks, have been used to distinguish among various types of coffee, fresh vs. spoiled fish, different types of wine, and mixtures of gaseous hydrocarbons. Despite all of this research prior to this effort, the sensing of gaseous mercury with a SAW device has never been proposed.

The use of a gold film to selectively sorb gaseous mercury is not a new technology. Many laboratory-based instruments, for example, indirectly measure aqueous mercury by bubbling air through a solution and collecting the mercury off gasses in a trap consisting of gold-coated sand granules. After all of the mercury has been bubbled out of the solution and amalgamated to the gold, the trap is subsequently heated, and the gaseous mercury is measured using optical techniques. Likewise, other sensing techniques have employed gold films, as well. The Jerome Instruments sensor,⁴ for example, employs a thin gold film and measures the electrical resistance of the gold-mercury amalgam. QCMs and acoustic plate mode (APM) devices have also typically utilized gold films to collect mercury. However, no existing approach has provided the combination of size, sensitivity, dynamic range and affordability of the proposed SAW mercury vapor sensor.

Commercial Potential of the Proposed Technology

Company Description

Sensor Research and Development Corporation (SRD) is a small business research and engineering company whose focus is to develop and commercialize sensors for industrial process control and environmental characterization and monitoring. SRD has been in business for over seven years and has a contract base that includes private industry, and state and federal government agencies. SRD interacts with various government agencies, academia, and private industry to identify the specific market demand for the product line that will be forthcoming from the proposed research and will focus future R&D activities on responding to that demand.

SRD is currently, or has been, involved in multiple related projects under State, Federal and private sector funding. These projects include funding for SMO films to detect and quantify chemical warfare agents (DOD), ammonia (DOE-METC), Fish Freshness sensor (NSF), medical diagnostics based on NO detection (NIH SBIR), and private sector support for the development of sensor components to control the Claus process for H₂S elimination in natural gas production (BOVAR Engineered Products). State funding has included research and development of a prototype NO medical instrument, corrosion monitors, and the development of improved sensor

instrumentation. Internal R&D activities include the development of films and devices for the detection of mercury, methane, mercaptans, hydrogen sulfide, and the oxides of nitrogen. Additionally, SRD is developing new optical techniques for the dissociation of gases at the surface of the thin film gas sensing elements. SRD is preparing for the commercialization of a fiber penetration monitor and an in-line temperature-humidity monitor.

Competitive Products

There are no existing products which provide the combination of size, sensitivity, dynamic range and affordability of the proposed SAW mercury vapor sensor. While existing QCM sensors are capable of ppm detection levels, the SAW sensor is capable of ppb and lower levels of detection. Thin film metallic sensors have claimed ppb detection; however they exhibit poor dynamic range (saturation / sensitivity). The only other detection methods for mercury which have similar sensitivity characteristics as the SAW sensor are mercury cold-vapor AA or AF instruments. Although these systems are highly accurate, they are not energy efficient and more expensive. ICP-AES has the required sensitivity but systems are still relatively large and complex. LIBS, a potentially *in situ* technique is difficult to calibrate and is not suitable for mercury detection in stacks due to the mercury self-absorption that occurs.

Current sampling methods (EPA Reference 29, Ontario Hydro Method) used to detect mercury require a variety of elaborate separation strategies in conjunction with chromatographic, electrochemical or spectroscopic methods such as atomic absorption and emission.^{1,41} Although these techniques are sensitive, they are batch processes and typically, samples are collected and shipped to a central processing facility for analysis.

McNerney et. al.³ demonstrated that the resistance of a thin gold film changes upon exposure to mercury due to the formation of a mercury-gold amalgamate. This chemiresistive type sensor later led to a commercial sensor produced by Jerome Instruments.⁴ This sensor utilizes a very thin gold film and has a limited dynamic range and sensitivity. Bristow¹⁴ and, later, other investigators^{14-18,28,29} demonstrated that a gold-coated quartz crystal microbalance (QCM) could also detect mercury. In this work the resonant frequency of the QCM changes due to the added mass of mercury on the gold film. A major drawback of the QCM mercury sensor is its relatively low sensitivity.

Commercialization

The technology and engineering available will enable a commercially viable sensor to be designed and packaged for applications which include industrial process control instrumentation, a hand held portable sensor for mobile site characterization and monitoring, and a standoff system for remote monitoring, data collection, and processing. Applications can be expanded as new films are engineered for different heavy metals and gases. Sensors will be warranted, maintenance and operational training will be provided, and field service/calibration options will be available. A full set of documentation will accompany sensor acquisition.

Funding under this contract will considerably enhance the commercialization of the sensor product line. Research and testing performed to this date has demonstrated the feasibility of the sensor including the reproduction of consistent and predictable films, the complete integration of the film with the SAW platform resulting in a pre-production sensor device with refined electronics suitable as process control instrumentation. The design, fabrication, materials and processes necessary to manufacture and commercialize a SAW-Hg sensor product line are the result of this effort to date. The development and incorporation of a suitable

sampling and preconditioning system will complete the development of the CEM. A test and evaluation (T&E) plan will be implemented and reliability and maintainability data will be gathered and evaluated. This will support the production of a sensor product line which requires minimal operational maintenance.

The SRD business development plan includes continued interaction with various government agencies, academia, and private industry to identify the evolving market demand for the sensor product line that will be forthcoming from the proposed effort and focuses internal R&D activities on responding to that demand. SRD conducts regular reviews with its investors and technical collaborators in order to identify the size and type of facilities, equipment and human resources required to fabricate, produce and manufacture a microsensor product line.

The Study

This topical report covers the period from May 1, 2000 through April 31, 2001 and provides a description of the present state of the development of an instrument for measurement of gaseous mercury in waste treatment processing facilities. The work previously performed under this contract was reviewed in mid 2000. Therefore only a brief summary of the work prior to the period under review will be given.

Description of the Technology

The underlying sensing mechanism for gaseous mercury is based upon surface acoustic wave (SAW) technology with a thin gold film used as an ultrasensitive microbalance. By coating the delay line with a thin gold film and configuring it as an RF oscillator, mass changes in the film can be measured by monitoring the oscillation frequency.

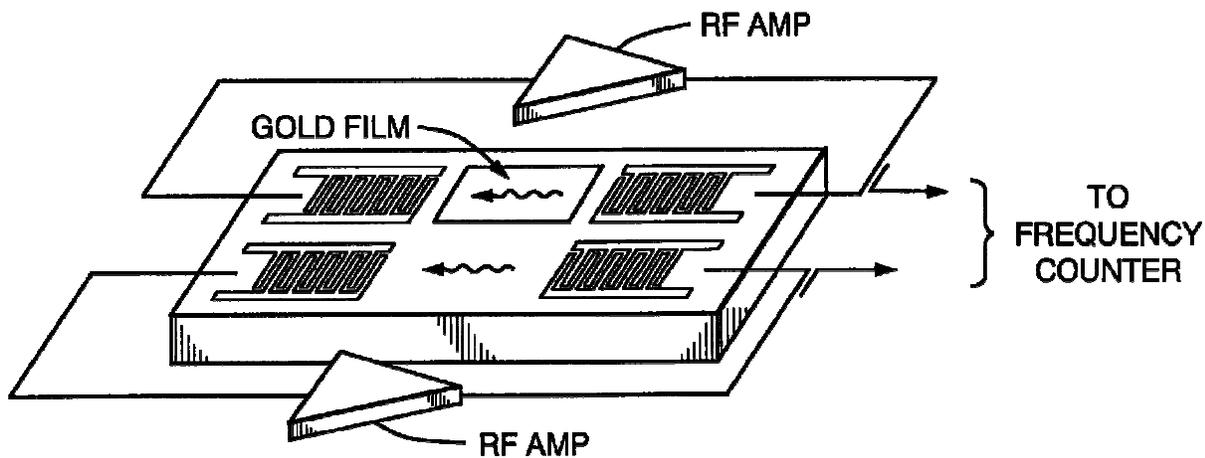


Figure 1. Schematic of the sensing element of the proposed SAW mercury sensor.

Because of gold's strong interaction with mercury (amalgamation), this configuration can be used to sensitively detect gaseous mercury. Mercury can be driven from the film by heating it to a high temperature. Furthermore, by operating the device at an elevated temperature, the

reaction kinetics of mercury amalgamation and desorption can be balanced so that an equilibrium surface mass can be quickly realized. The oscillation frequency then becomes a direct measure of the instantaneous mercury concentration. A second SAW delay line without a sensing film is also incorporated into the device to act as a reference so that extraneous environmental effects which perturb both delay lines equally (i.e. temperature fluctuations) can be subtracted out.

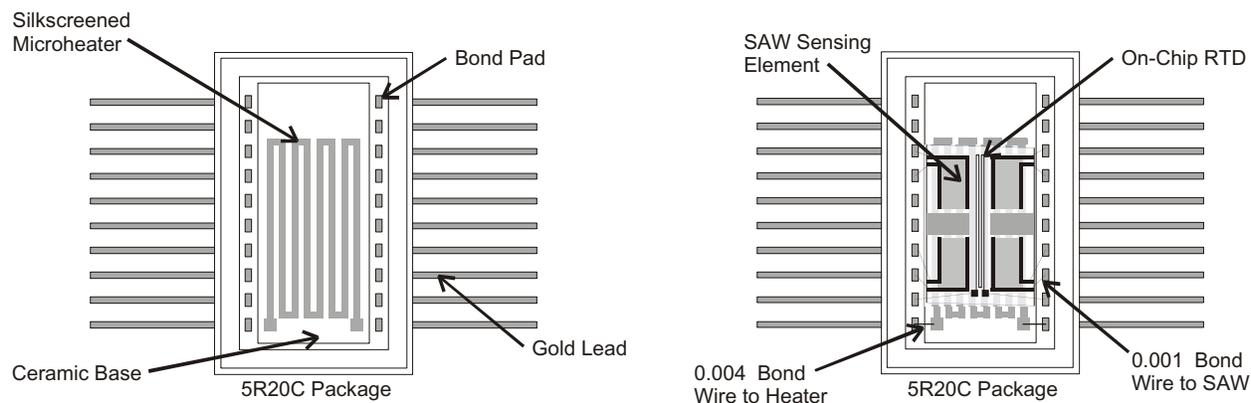


Figure 2: Schematic diagram of the sensor element design.

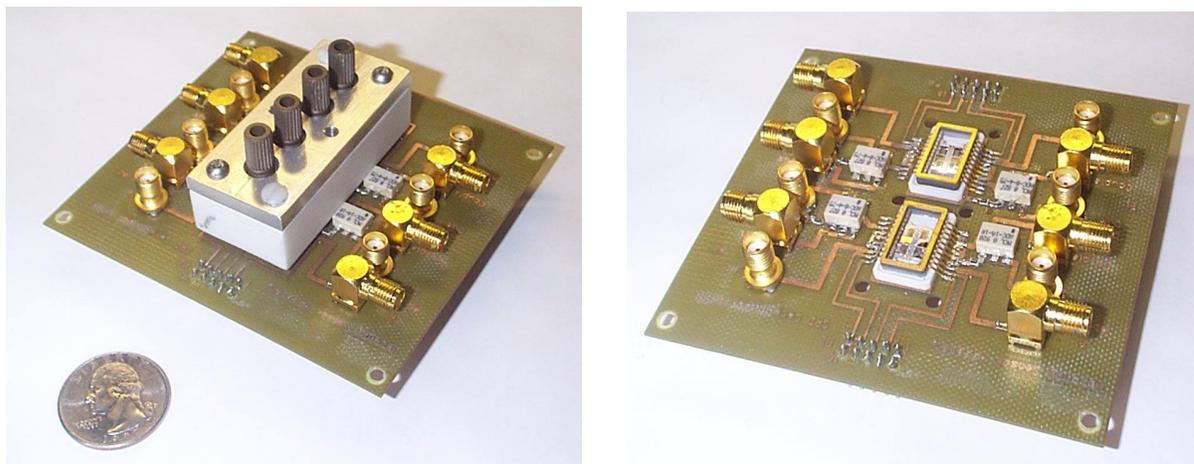


Figure 3: Modular Mercury sensing prototype package, with chamber (left) and without chamber.

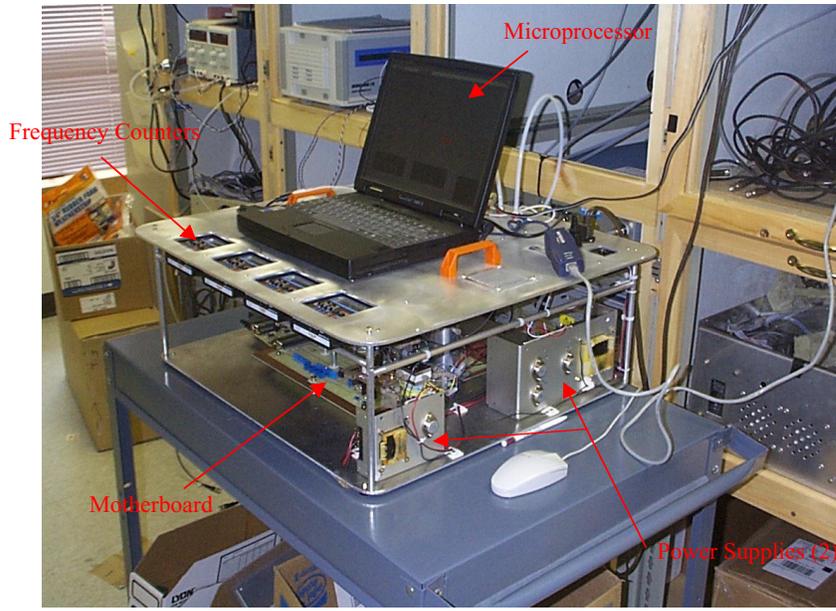


Figure 4. Completed Prototype Number 1 (Case not shown)

Requirements for the design of the prototype instrument were determined by a review of the current literature, comparison with competing technologies, consultation with DOE and contractor personnel, and consultation with personnel at the University of North Dakota, Energy and Environmental Research Center. A basic instrument design was developed that had the following characteristics:

- 1.) Two independent SAW sensor elements were employed, alternately sampling the stack gas path. This allowed one of the sensors to desorb, while the other was taking an active sample.
- 2.) Sample filters and gas handling would be configured such that the filters could be periodically backflushed, maximizing filter life and minimizing the scavenging effect of particulate in the filter.
- 3.) As a concept demonstrator, the instrument was portable, but was not optimized for size or weight. Use of commercial off the shelf hardware and software simplified the construction of the instrument, and allowed the emphasis to be on the development of the SAW sensor technology.
- 4.) The instrument could be remotely operable.

Operating Temperature

The initial goal of an *in situ* sensor required the sensor elements to be heated. Most of the initial testing with prototype 1 was conducted with an operating temperature of 150 °C and a desorption temperature of 165 °C. At this elevated temperature, mercury is being constantly integrating effect of the sensor elements. desorbed as well as absorbed. Difference frequency data from an early test showing the individual detector response to 27 µg/m³ elemental Mercury in dry nitrogen is contained in shown in Figure 5. The effect of chopping the gas stream is evident in the plots.

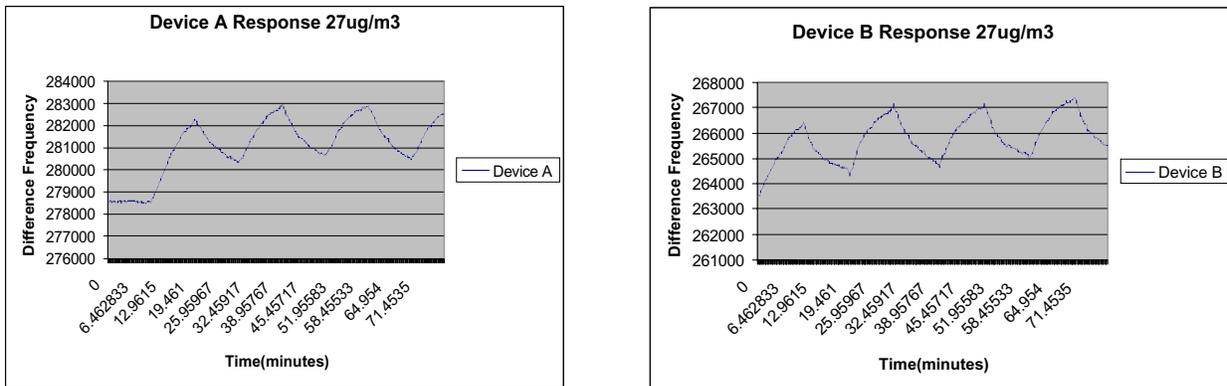


Figure 5. Individual sensor response.

The goal of this work was to establish the correct combination of slope and trend information that would be processed to provide a continuous concentration output at update rates greater than 1 per minute. Testing determined that changes in responsivity varied as a function of the long-term average Mercury concentration. That is, the slope was not a reliable indicator of concentration under these operating conditions. A signal-processing algorithm was developed based on the DC response of the sensor. This resulted in slower response than using the slope (5-15 min typically), but less sensitivity to noise. An instrument program incorporating variable cycle time between flow paths based on peak response, dead time (to eliminate transients) and operating temperature was written. This program also allows the setting of the desorption temperature (the temperature of the sensor during the desorption cycle) to be independent of the operating temperature.

Numerous test runs were made to characterize and calibrate the response of both sensors. Since the sensor response was non-linear, an evaluation was made to determine the best function to fit to the response curves. The best performance during this early testing was obtained with a piecewise quadratic, with concentrations above and below $\sim 50 \mu\text{g/dscm}$ being fit to 2nd order equations. Based on this calibration, the instrument was tested in chopped (variable cycle time) and pseudo-continuous mode using elemental Hg concentrations of 10-200 $\mu\text{g/dscm}$.

In chopped mode, the instrument monitored the slope of the active sensor until the peak (zero slope) was detected and recorded the corresponding concentration. This represented the equilibrium value of the sorption and de-sorption rates of the sensor and is proportional to concentration as seen by the sensor. During the exposure, the temperature of the alternate sensor heated sufficiently to ensure the complete de-sorption of mercury before the flow path was switched. In continuous mode the flow path was switched at an arbitrarily long (in this case 120 minutes) time and the concentration value was taken once per minute. The alternate sensor was again heated to ensure complete de-sorption. In the chopped mode, the flow path-switching transient was manifested as a lack of repeatability from exposure to exposure. The continuous mode did not have the short term variability displayed in the chopped response, but did exhibit significant long-term drift due to the same noise sources.

The decision to use the UNDEERC sampling and preconditioner as the sampling interface for the SAW sensors solved these problems by removing the requirement to operate the sensors at elevated temperature. This allowed the mercury measurement to occur near ambient temperature where desorption processes are negligible and the sensor can be completely desorbed at high temperatures between measurements. Under these conditions, the sensor response is directly related to the mercury exposure with noise and long-term drift substantially reduced.

Speciation

In addition to gaseous elemental mercury, the contract modification of December, 1998 required the study of mercuric chloride (HgCl_2). A delivery system was built and tested. The results of this work were reported in the Topical Report for the period of October 1, 1997 through March 15, 1999 which was covered in the last ASME review of this project. Briefly, the SAW sensor was observed to respond to HgCl , but the concentrations could not be verified since the SRD CVAFS does not respond to HgCl . Therefore, verification of HgCl response was to be performed during the initial UNDEERC field test. Unfortunately, damage to the instrument in transit to UNDEERC prevented this experiment from being performed.

With the DOE request to use the UNDEERC preconditioner & sampling system (output is completely elemental mercury), this effort was discontinued during the present stage of development.

Interference Effects

It is well known that, although relatively chemically inert, gold films can be poisoned.⁴³ This fact was clearly demonstrated during an interferent test undertaken by SRD at NDERRC on March 20-22, 1999 (see Figure 6). The original test matrix called for combinations of four interferents in a base gas mixture as shown in Table 1. The order of tests was arranged to place the HCl test at the end of testing, since this was a known poisoning effect.

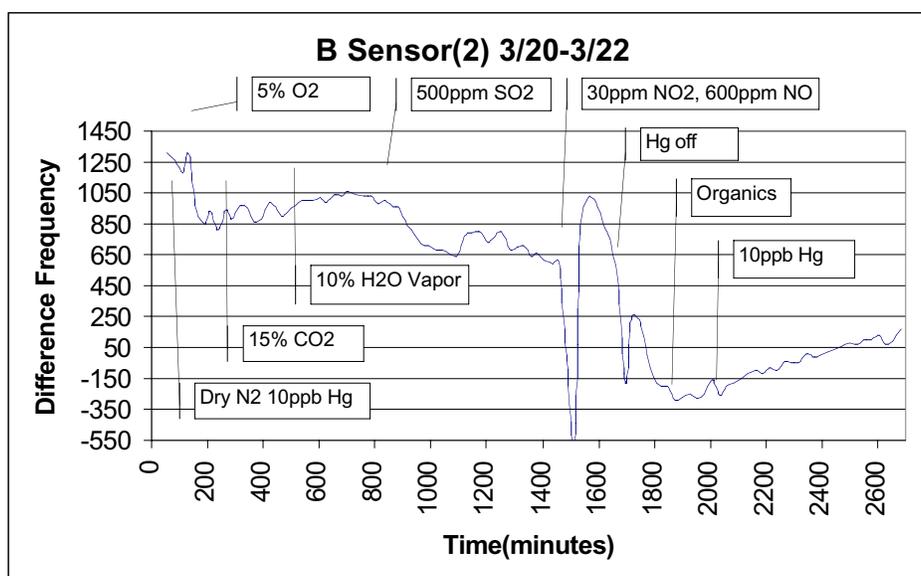


Figure 6. Sensor response when exposed to potential interferences. (Test 3/20/1999).

Test No	SO ₂	NO/NO ₂	HCl	Organics
1	500	600/30	500	5
2	0	600/30	500	5
3	500	0	500	5
4	0	0	500	5
5	500	600/30	0	5
6	0	600/30	0	5
7	500	0	0	5
8	0	0	0	5
9	500	600/30	500	0
10	0	600/30	500	0
11	500	0	500	0
12	0	0	500	0
13	500	600/30	0	0
14	0	600/30	0	0
15	500	0	0	0
16	0	0	0	0

Table 1. Bench scale interferent tests (ppm). The base gas stream included 5% O₂, 15% CO₂, 10% H₂O vapor, with the balance N₂.

The gas delivery system was configured for the base gas stream, 500ppm SO₂, and 5ppb Hg.

The following observations (see Fig. 6) were made about the operation of the SAW Mercury sensors as a result of this field test.

- After exposure to the base gas (5% O₂, 15% CO₂, 10% H₂O vapor, Balance N₂) the instrument output was erratic, indicating that the two sensor packages were not responding the same.
- Long term exposure to the base gas stream resulted in an irreversible 50% reduction in response to elemental Hg. This is in addition to the calibration error mentioned above. (R reduced to <100 Hz/ppb Hg).
- 500 ppm SO₂ in the presence of the base gas and 5ppb Hg caused a negative, persistent response of between 500 and 1000 Hz (subtracting from the Hg response).
- 600 ppm NO/30 ppm NO₂ in the presence of 500 ppm SO₂, the base gas and 5ppb Hg caused a large negative transient response (>1 kHz).
- Introduction of organics in addition to the above gases was not detectable. (The sensor may have been dead by this point so this is not conclusive.)
- Introduction of 500 ppm HCl in addition to the above gases resulted in an immediate response of ~ 9 kHz. The sensor did not appear to be operational after this exposure, even after long exposure to Dry N₂ only.

Although the prototype instrument was damaged in transit, it was clear from the results obtained that the sensor was very sensitive to some of the interferences that would be encountered in exhaust gases. Although further experiments eliminated some of these interferences (e.g. SO₂, NO_x) as the cause of the problem, DOE requested SRD to incorporate

into future tests a UNDEERC sampling and gas preconditioner that was, at the time, under development at the University of North Dakota's Energy and Environmental Research Center (UNDEERC) to eliminate any interference problems.

As previously noted, this decision had a number of effects on the research project. With the interferences removed and the mercury present in the sample converted to elemental mercury, the SRD mercury SAW device was now only required to measure elemental mercury at room temperature. Taking these operating conditions into account, the design of the sensor was modified to operate at optimum sensitivity.

Film Thickness

One piece of information that is essential to the use of gold coated SAW devices to measure mercury concentration is an understanding of the loading of the sensor with mercury and the effect this loading has with respect to the apparent frequency change. The questions that were addressed included: Is the change in frequency response linear? If so, over what range does it remain linear?

To begin to answer these questions, a series of experiments were undertaken to monitor the frequency response with time for a range of film thickness and mercury loading. Figures 7, 8, and 9 summarize the results that were obtained from this work. Figure 7 gives the 1st derivative for a 15 μ m gold SAW exposed to increasing gas flows containing increasing mercury concentrations. The response is clearly dependent on both time and concentration. Figure 8, on the other hand, demonstrates both the response and 1st derivative of a 500 μ m gold film SAW sensor. In the thicker film the initial response of the sensor, as shown by the plot of the 1st derivative, becomes non-linear. Evidence suggests that this response is due to an additional stiffening factor that can occur in thicker gold films when they are exposed to mercury. This stiffening results in an opposite change in frequency to that induced by the mercury loading. Such responses introduce significant complications into the data analysis that effectively eliminate thick films from use in this application. The overall result of these experiments indicated that a gold film having a thickness of 75 μ m and an operating temperature of 30 $^{\circ}$ C is the optimum in terms of both linear response and loading. The linear response of such a sensor can be seen in Figure 9. For this film thickness, a detection limit of 0.6 μ g/dscm was established.

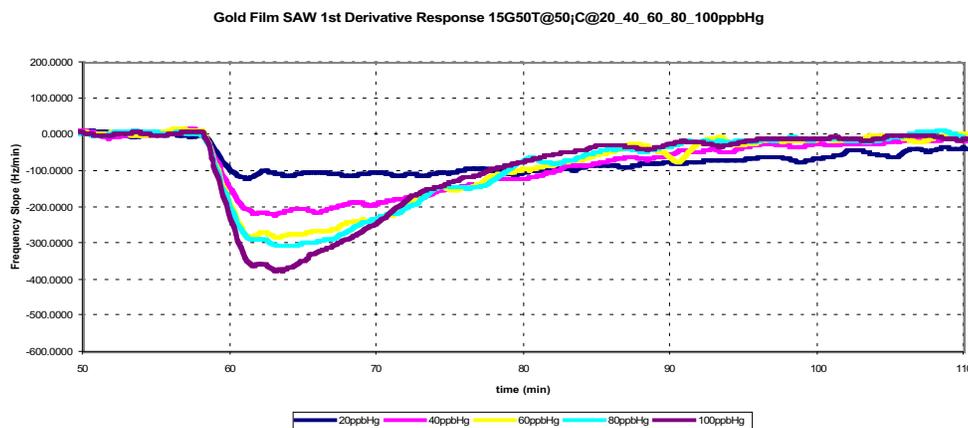


Figure 7: The 1st derivative response of a 15 μ m gold film SAW sensor to various mercury concentrations.

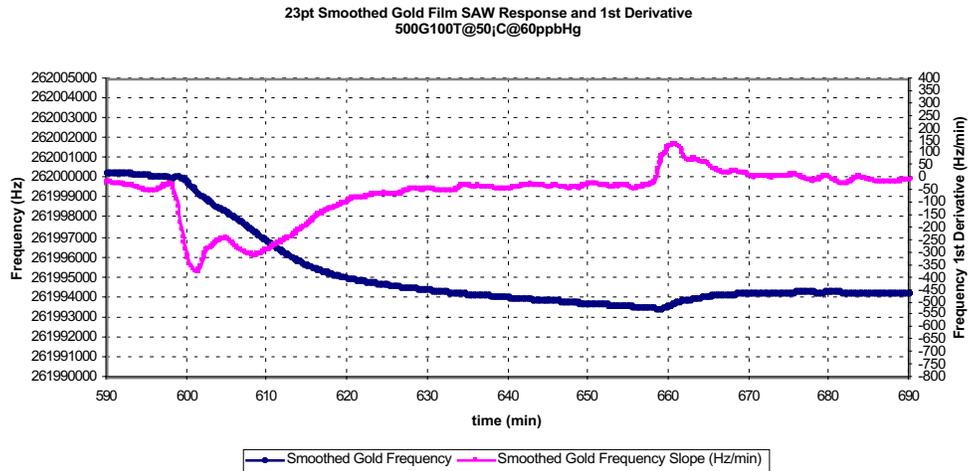


Figure 8: The response and 1st derivative of a 500 gold film SAW sensor when exposed to 7.3 $\mu\text{g}/\text{dscm}$ over 60 minutes.

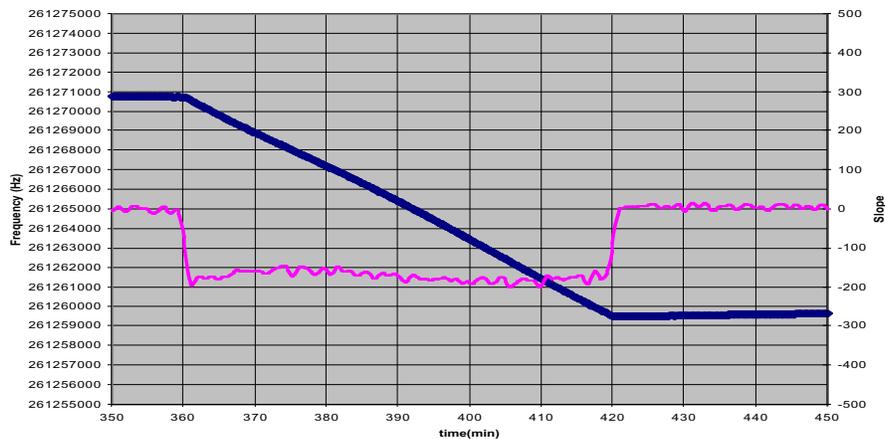


Figure 9: The response (thick line) and 1st derivative of a 75 Gold film SAW sensor exposed to 2.5 $\mu\text{g}/\text{dscm}$ of mercury over 60 minutes.

Present Status

As mentioned above, the decision to integrate a gas preconditioning system into the sensor instrumentation alleviated the requirement for high-temperature operation, as the output from the preconditioner would be near room temperature. By operating the sensor at low temperatures, higher sensitivity is achieved due to the higher collection efficiency. To take advantage of the change in operating conditions, the instrument was redesigned. In particular, the instrument was designed to be modular in all aspects, including measurement electronics, filters, and pumps. The new design, while based on the original electronics, allows the simultaneous testing and independent temperature control of up to four SAW dual delay line sensors. Individual sensors are desorbed by heating to 150 °C, cooled to 30 °C, and then exposed to the gas stream. Once exposed, this cycle is repeated. This cycle provides maximum stability,

repeatability and sensitivity. Individual sensors have been cycled continuously for days at a time. The sensors have lasted for periods exceeding six months under this regime.

In terms of field use, it is envisioned that three of the sensors would be used sequentially to monitor low level mercury emissions. One sensor would be monitoring the gas stream, one channel would be regenerating and the third would provide backup, ready to take over if a large spike swamped the operating sensor. The flow through the fourth sensor would be set to allow it to quantify any large mercury spikes that may occur during waste treatment.

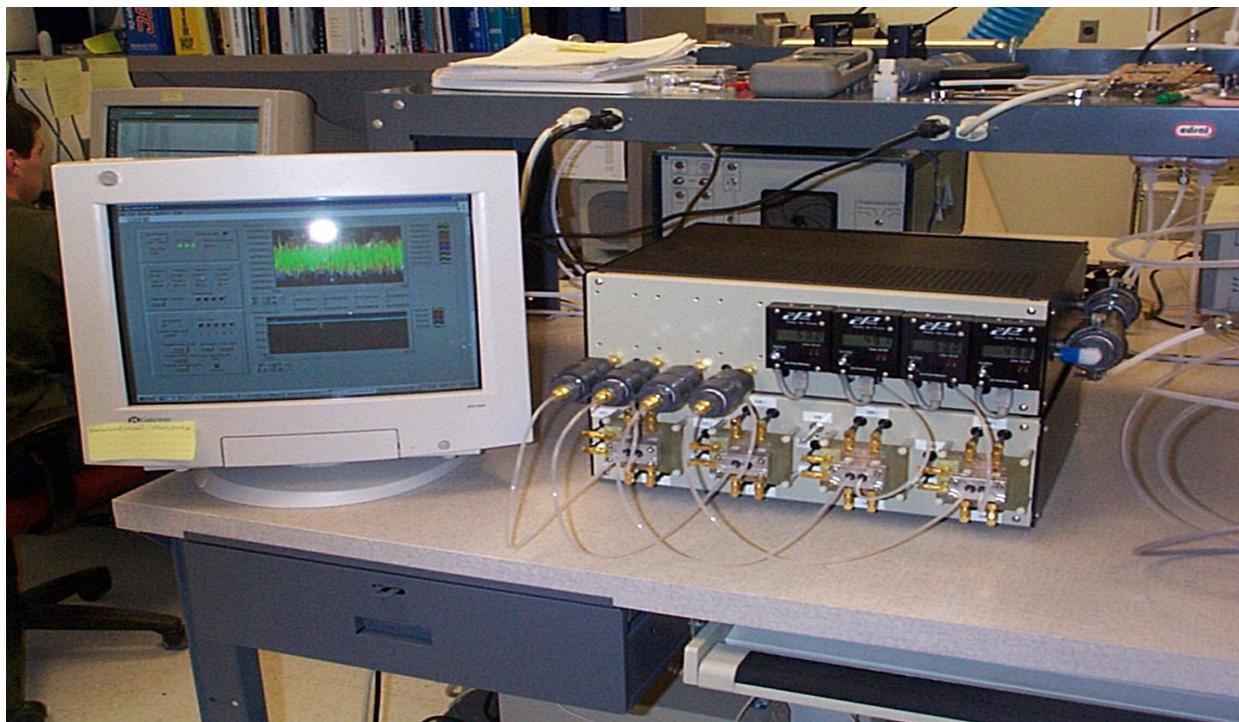


Figure 10. Photograph of the new apparatus for simultaneous measurement of four SAW sensors.

Software was modified to allow for the operation of the eight SAW delay lines either sequentially or simultaneously. A photograph of the new setup is shown in Figure 10.

A LabView software program that has been developed to control the eight individual SAW devices that makes up the Multi-Channel SAW Mercury Monitor. A printout of the screen is given in Figure 11. As the software is LabView-based it can be configured to display frequency, slope, or mercury concentration in dscm (@ 7%) as required.

Sampling System:

For continuous sampling, a multi-channel sampling system capable of providing individual gas flows to each channel of the multi-channel SAW sensor was developed and tested (see Figs. 12 & 13) to interface with the UNDEERC sampling system. As the schematic diagram indicates, the sensing elements can be operated in series or parallel. To allow for sensor regeneration, gas flowing to the sensor being regenerated was passed through a charcoal filter to remove mercury while the other flow path remained unfiltered.



Figure 11: A screen printout of the computer display of the multi-channel sensor operating software.

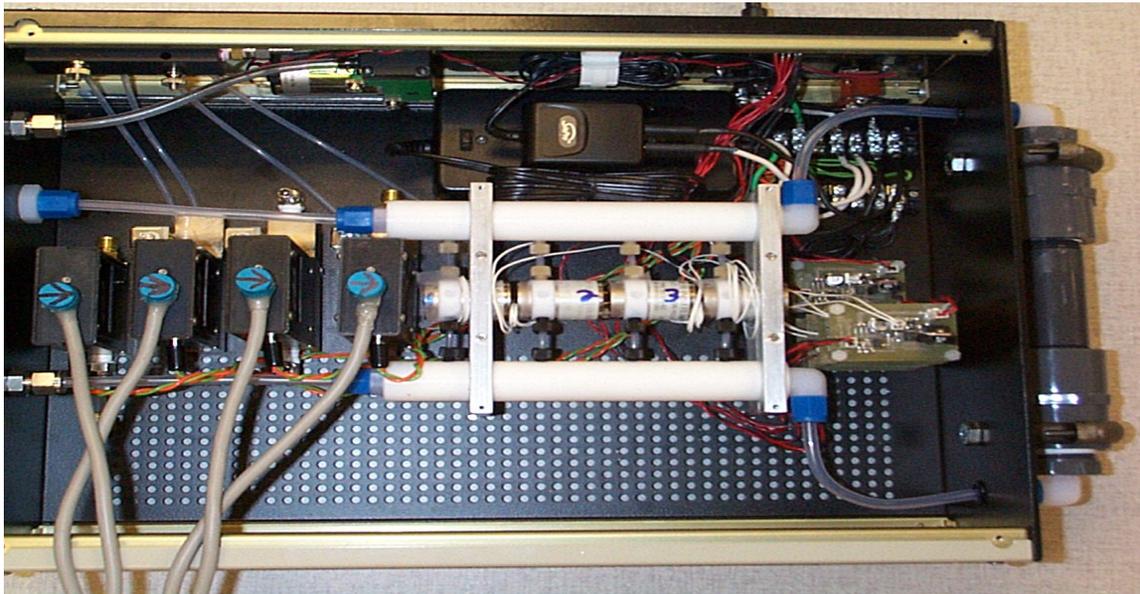


Figure 12: Photograph of the multi-channel sampling system.

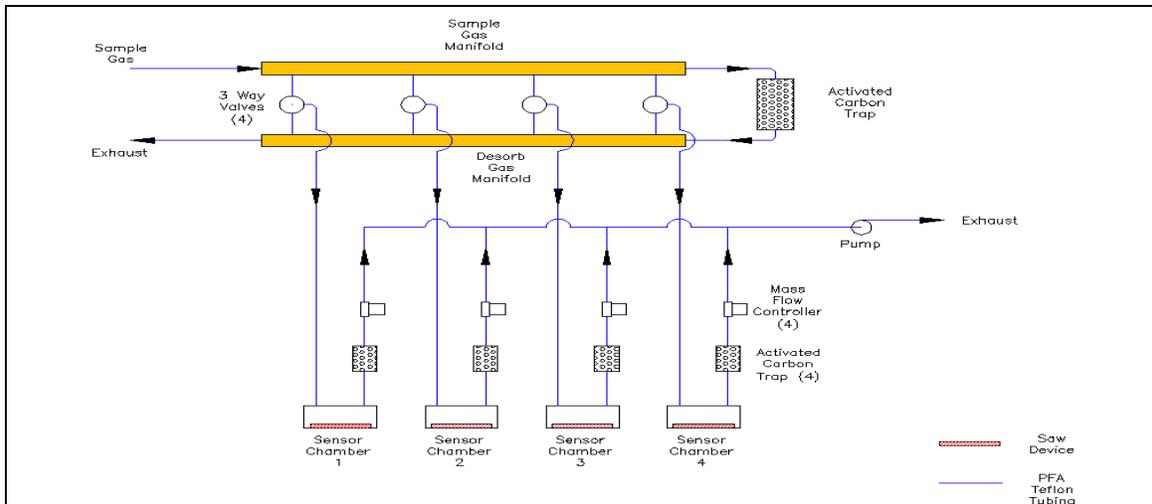


Figure 13: Schematic diagram of the multi-channel sampling system.

The two gas streams can be switched between the sensing elements thereby allowing a periodic baseline measurement to be made for each sensing element without interrupting mercury measurement of the overall instrument. Activated carbon filters remove any mercury in the gas stream before it exhausts the system.

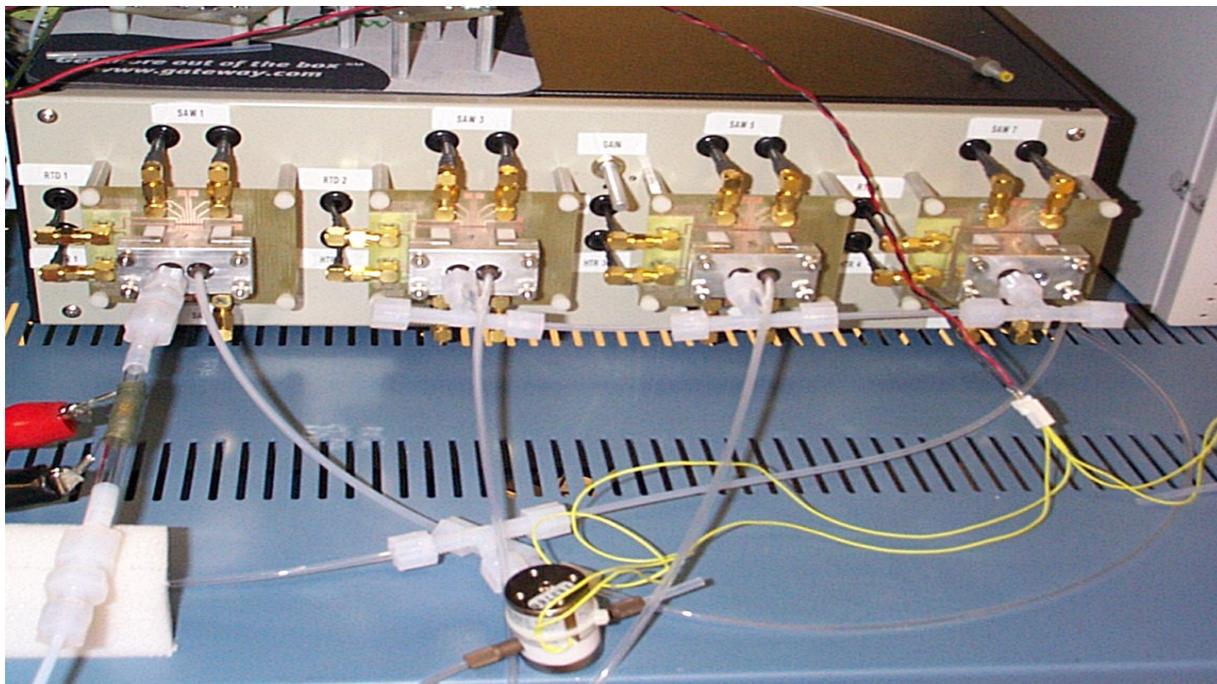


Figure 14. Photograph of the gold trap experiment using one channel of the multi-channel Mercury SAW Monitor.

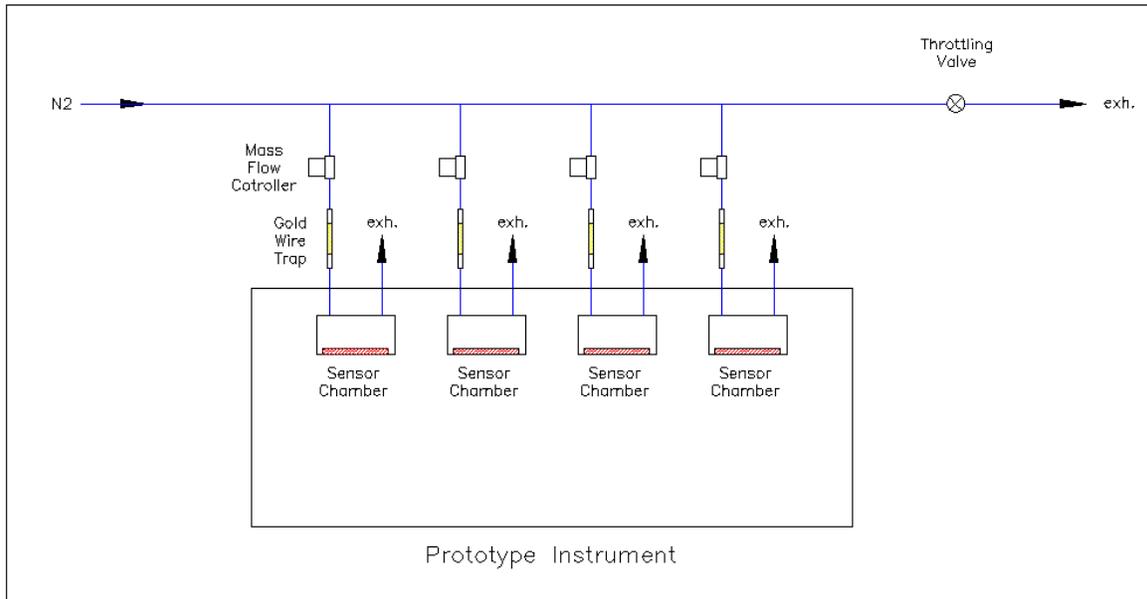


Figure 15: Setup for Hg Spike Tests.

Spike Testing

One method of monitoring low levels of mercury is by preconcentrating the mercury onto a gold trap. The mercury is then evolved completely off the gold trap by rapid heating in approximately 30 seconds or less resulting in a short sharp mercury spike. This method has the advantage of producing a large signal but at the cost of not being able to continually monitor a gas stream in real-time. Figures 14 & 15 are a photograph and schematic of the instrument configured for measuring mercury spikes.

The SAW sensor has been designed to monitor low levels of mercury ($1-2 \mu\text{g}/\text{m}^3$) continuously, however, the potential exists in DOE waste treatment facilities for large spikes of mercury to occur. The question is: Can the SAW sensors monitor such spikes? To address this concern, a series of experiments were performed to establish the behavior of the SAW sensor. That is, the effect of short sharp mercury spikes was measured and the operating conditions optimized for the present SAW sensor. In addition, notwithstanding the presence of the NDEERC gas conditioner, this approach also avoids the possibility of interferent gases poisoning the sensors and ensures a full evaluation of the instrument during the field test. At mercury concentration levels of approximately $1-2 \mu\text{g}/\text{dscm}$ one would expect to see frequency changes in 3000-5000 Hz range for a loading of 5 ng, when the SAW sensor is sampling continuously. However, as can be seen in Figure 15, the short (~30 s) spike that is evolved from a gold trap loaded with 5 ng of mercury gave rise to a frequency change of approximately 300 Hz.

In measuring transient mercury spikes, factors that would be expected to impact the sensitivity of the sensor would be the residence time and reaction efficiency. Both of these factors depend upon the flow rate of the sample across the sensor. The results of an experiment

showing the sensor response with respect to flow rate can be seen in Figure 16. It is clear that the sensor response drops rapidly with increasing carrier flow. This dependency of the sensor sensitivity on flowrate, together with multi-channel capability, allows the instrument to be operated such that one channel can be optimized to monitor large mercury spikes (potentially mg/dscm levels) while the other channels have the sensitivity to continuously monitor low mercury concentrations.

With the present instrument design, an optimum flowrate to maximize sensitivity for the measurement of transient mercury spikes was found to be 8 cc/min with a resulting increase in sensitivity from 300 (100 cc/min) to over 2000 Hz.

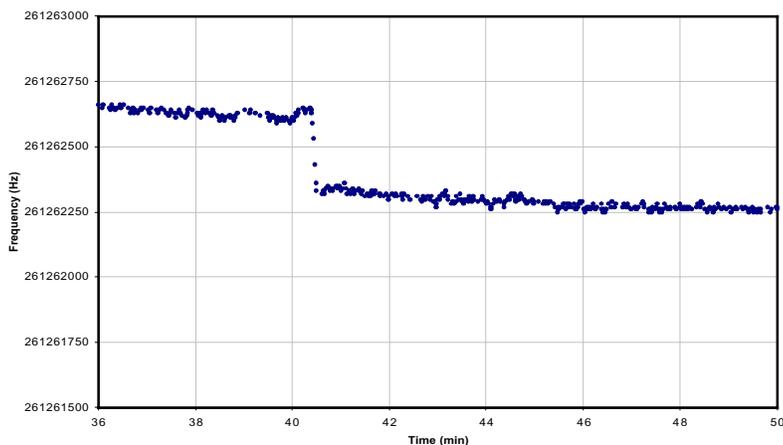


Figure 15: SAW sensor response to a 5 ng Mercury spike from a gold trap. Gas flow rate 100 cc/min.

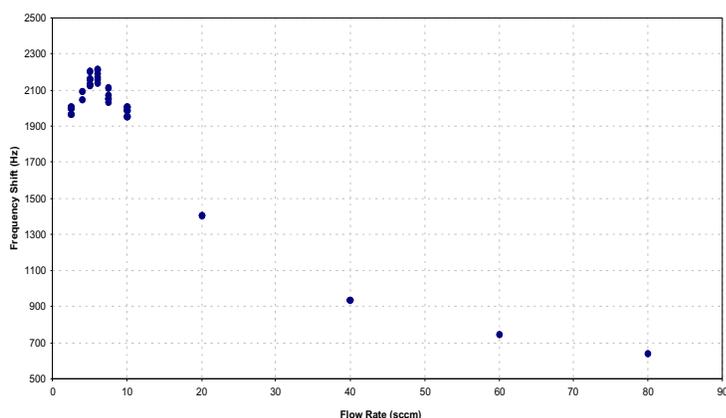


Figure 16: The frequency shift of SAW sensor with respect to Nitrogen Flow Rate. Mercury load 14.2 ng.

One piece of information that is essential to the success of the SAW device to measure mercury concentration is an understanding of the loading of the sensor and the effect this loading has with respect to the apparent frequency change. That is, is the change in frequency response linear? If so, over what range does it remain linear? Figure 17 shows the calibration curves for three different sensors. A series of spike measurements made at varying mercury loads, starting a 2.5 ng and increasing to 35 ng. This shows that the sensor response of each sensor is linear over the range measured and that under these conditions, the detection limits for the 75 Å films were 9.8 and 9.9 µg/dscm respectively and repeatability was within 2%. As the sensor saturate, the curve rolls off and the response becomes non-linear. For the 75 Å thick films, this occurred at loads in excess of 45 ng.

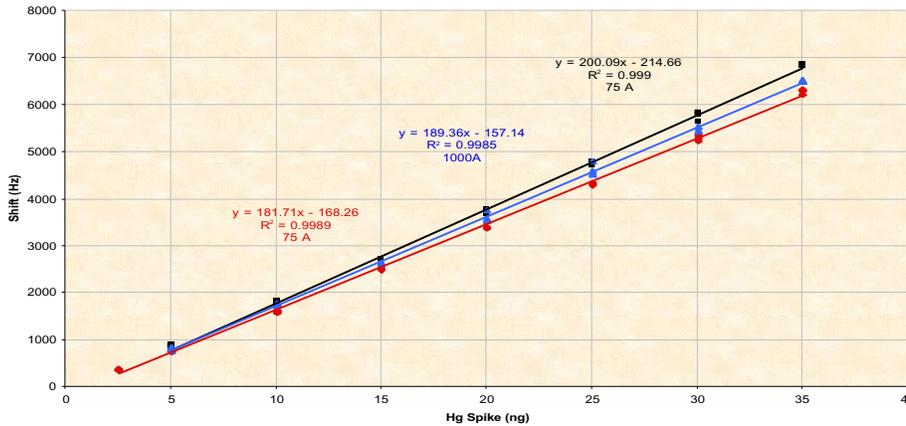


Figure 17: Calibration curves for two 75 Å and one 1000 Å thick Gold SAW sensors. Flow rate 8 cc/min.

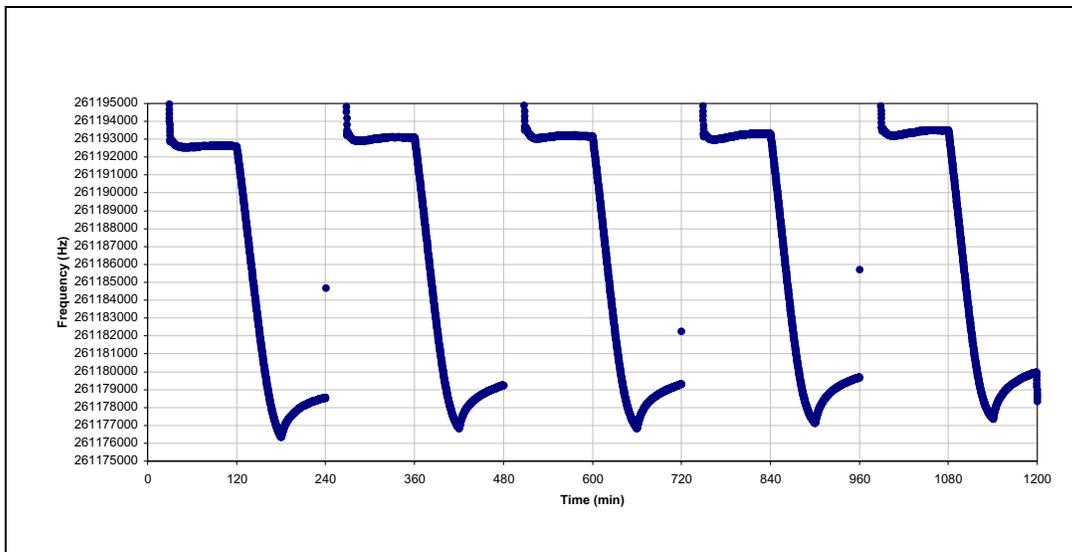


Figure 18: Repeat cycles of exposures and desorption of a SAW sensor to a continuous flow (N_2) of mercury at a concentration of 1.2 µg/dscm.

Continuous Tests

A series of experiments were performed with the sensor in continuous sampling mode. Figure 18 demonstrates the repeatability and sensitivity (frequency shift 17kHz over a time period of 60 minutes) of this approach. As can be seen the measurements are highly repeatable.

It should be noted that the actual mercury concentration measurement is determined from the slope. Figure 19 is a plot of slope versus concentration and integrating over one minute yielded a detection limit (DL) of 0.6 $\mu\text{g}/\text{dscm}$ with a precision of -3% .

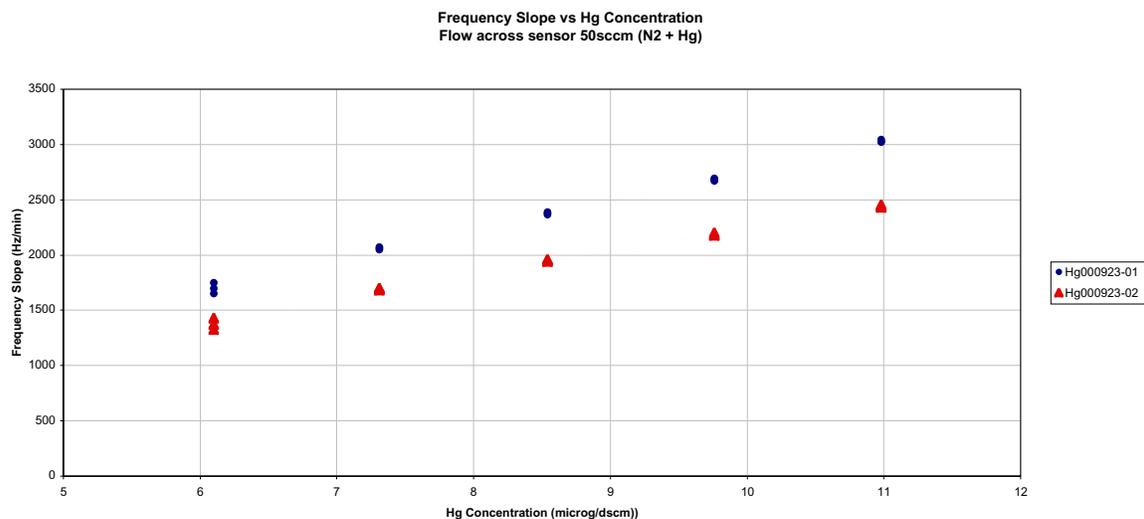


Figure 19: Plot of slope versus Mercury Concentration for Continuous Sampling

UND-EERC Field Test

A field test of the Hg SAW instrument was arranged to take place at the North Dakota University EERC for the week of March 12, 2001 and a test plan was developed (see below).

Hg North Dakota University EERC Test Plan — March 2001

Monday March 12th

- Unpack and setup instrument.
- Perform instrument check and begin instrument calibration (if time allows).

Tuesday March 13th

- Calibration: Calibrate instrument using UNDEERC permeation tube. Load the gold traps (at 5ng intervals) starting at 5ng, up to 35 ng. Repeat for each sensor.

Begin spike tests. Load gold traps with samples being taken from the output of the UNDEERC gas sampling and preconditioning system. Compare results with UNDEERC Semtech Hg 2000 AA. Repeat for each sensor.

Wednesday, March 14th

Complete spike tests.

Set up instrument to interface directly with output of the UNDEERC sampling and preconditioner to demonstrate continuous sensor operation & evaluate sensor behavior.

Single sensor only,

- 1) Introduce only O₂, CO₂, and H₂O (balance N₂) through preconditioner.
- 2) Add all interferent gases

Evaluate sensor performance: Subject to sensor response either continue with continuous sampling and determine the viability of calibrating, monitoring drift, etc. by spiking using either gold trap or head space injections. Add additional sensor and cycle sensors sequentially.

Thursday, March 15th, Continue Continuous Test

Friday, March 16th

Complete testing (if necessary) & pack instrument for shipping back to SRD.

UNDEERC Testing Facility

A full description of the UNDEERC sampling and gas preconditioner system is outside the scope of this report. However, a brief description is necessary. Figures 20 and 21 are a schematic diagram and a photograph of the UNDEERC sampling and gas preconditioner respectively. Table 2 lists the interferent gases that are introduced into the preconditioner and the stated output of the system.

Interferent Gases Into Conditioner	Interferent Gases Out of Conditioner
6% O ₂	6% O ₂
12% CO ₂	12% CO ₂
1600ppm SO ₂	0
50ppm HCl	0
300ppm NO	300ppm NO ?
20ppm NO ₂	20ppm NO ₂ ?
8% H ₂ O	0

Table 2: Input versus Output of Interferent Gases of the UNDEERC sampling and preconditioning system.

Mercury Supply

Hg Permeation rate (certified): 195 ng/min.

Flow across permeation tube: 3303 sccm N₂ (7.00 cfh).

Total flow from Conditioning System: 8928 sccm N₂, (15 scfh).

Gold traps are loaded with 45 sccm slipstream.

Unfortunately, there was no way at the time of the field test to experimentally determine the actual composition of output gas from the preconditioner of the introduced gases. The output was clean enough to allow the mercury concentration to be monitored using a Semtech Hg 2000 AA and a PS Analytical Sir Galahad CVAF.

Spike Test Results:

The instrument was set up in a similar arrangement to that depicted in Figure 12 above. A series of mercury spikes ranging from 5 ng to 35 ng was loaded onto gold traps both directly from the permeation tube (i.e. traps were loaded with N₂ carrier + Hg only) and from the output of the sampling and preconditioner system (traps loaded with N₂ carrier + Hg + Interferent gases). Figures 23 & 24 are the calibration curve (frequency shift versus mercury load) for two SAW sensors. Figures 25 and 26 compare the results obtained by the SAW sensors and the Semtech detector.

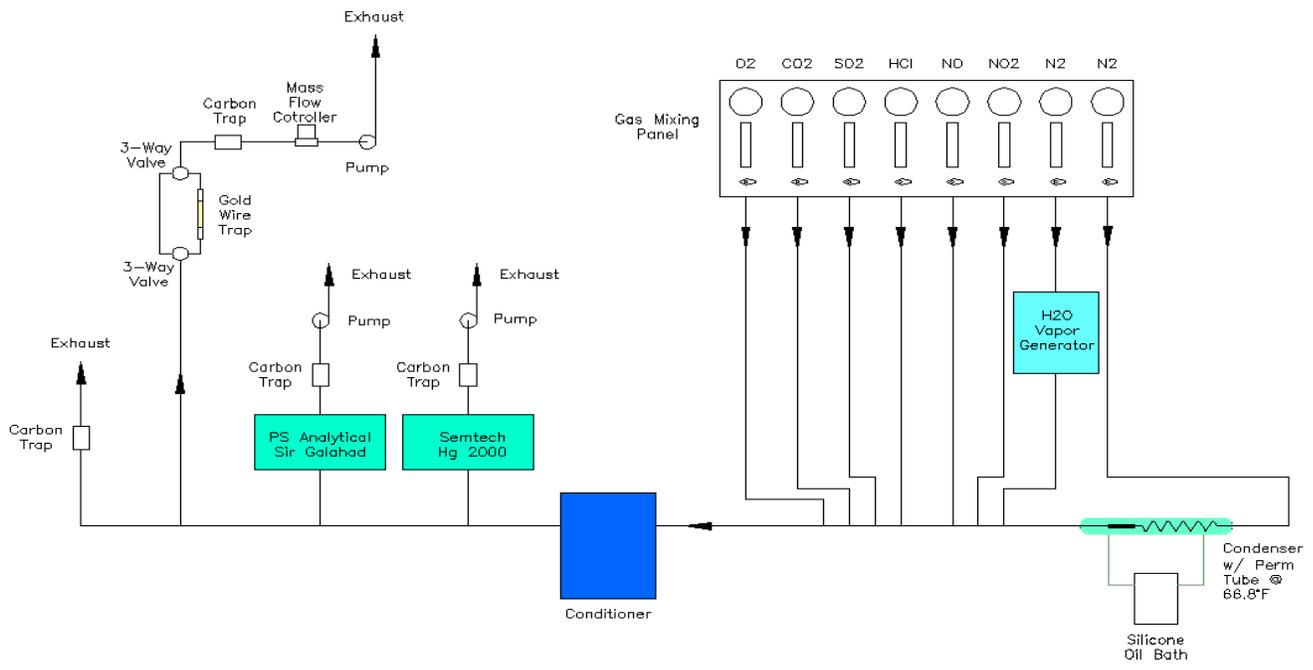


Figure 20: UND-EERC Gas Delivery System with setup for loading gold wire traps.

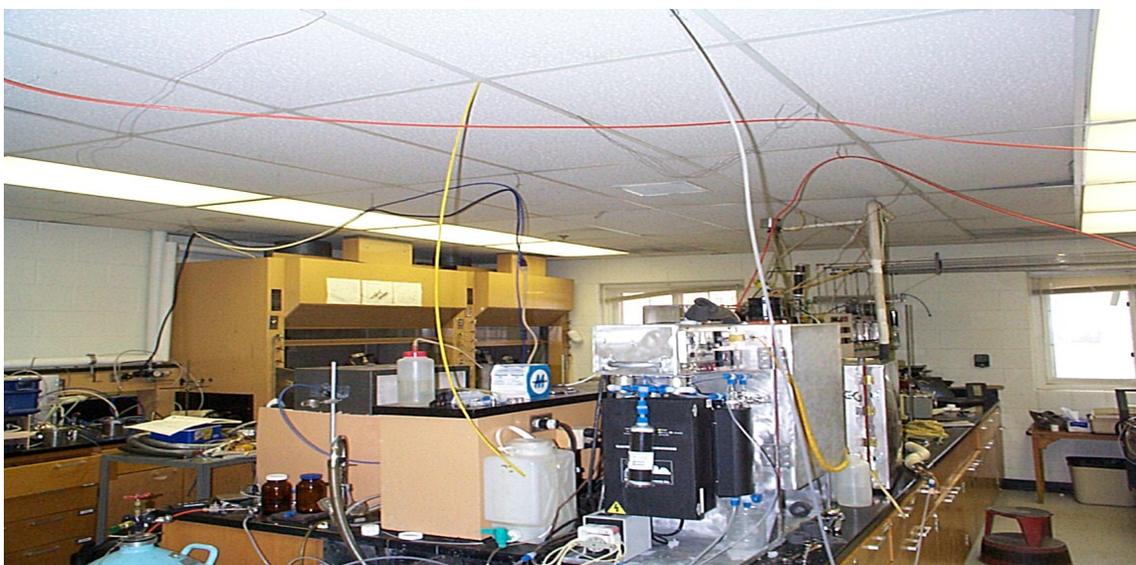


Figure 21: UNDEERC Gas Preconditioner

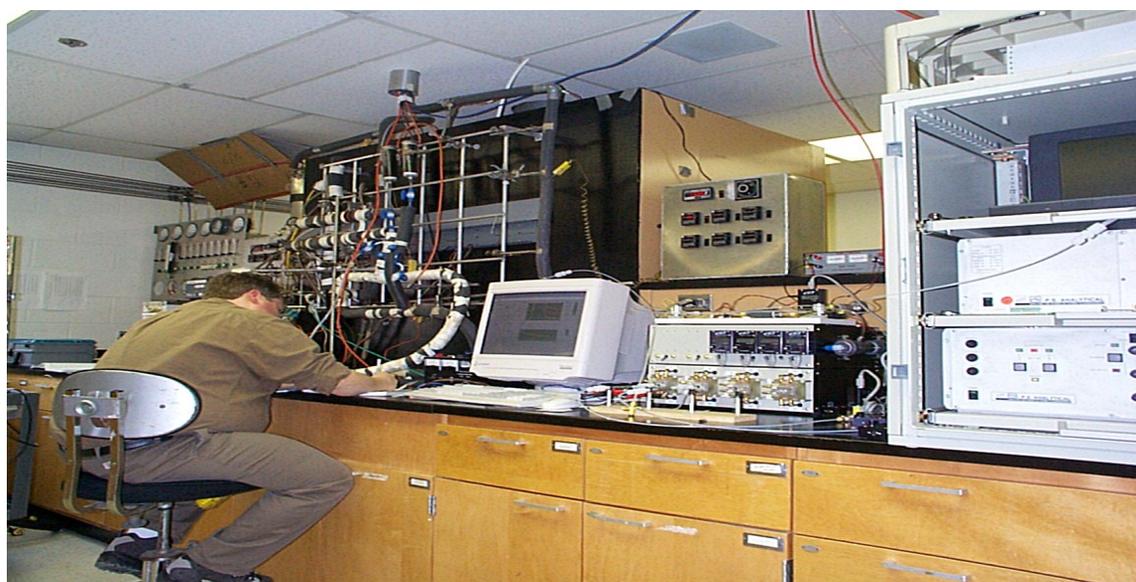


Figure 22: SRD's Mercury SAW-based Detector at the UNDEERC.

The shift in frequency of the SAW sensor is used to obtain the mercury load on the gold trap from the calibration curve for each sensor. The Semtech Hg 2000 measurement is the average mercury concentration measured during the loading of the gold traps plotted against the frequency shift seen by the SAW sensor. The results of the SAW sensors are more repeatable with less scatter. This may be due to the fact that the semtech only provided an update every minute. Nevertheless the results are in excellent agreement (Fig. 25, 26) with all the results within -5% . The results also indicate that, over the period of the test (~ 2 days), no poisoning effects were observed. This conclusion is supported by the individual responses of the sensors before and during (Figure 27) the field test.

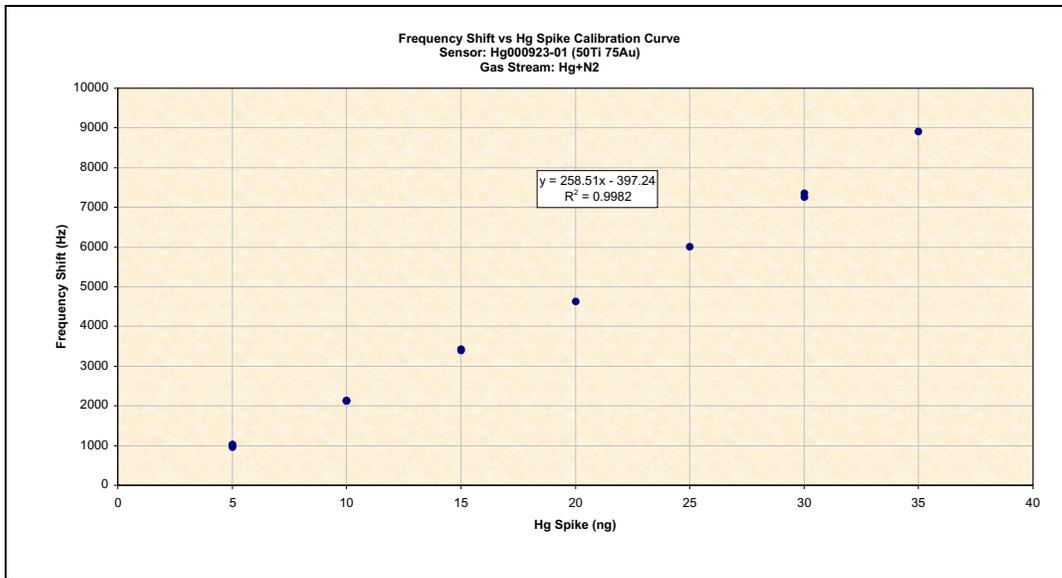


Figure 23: Saw Sensor 1 - Mercury Spike Calibration.

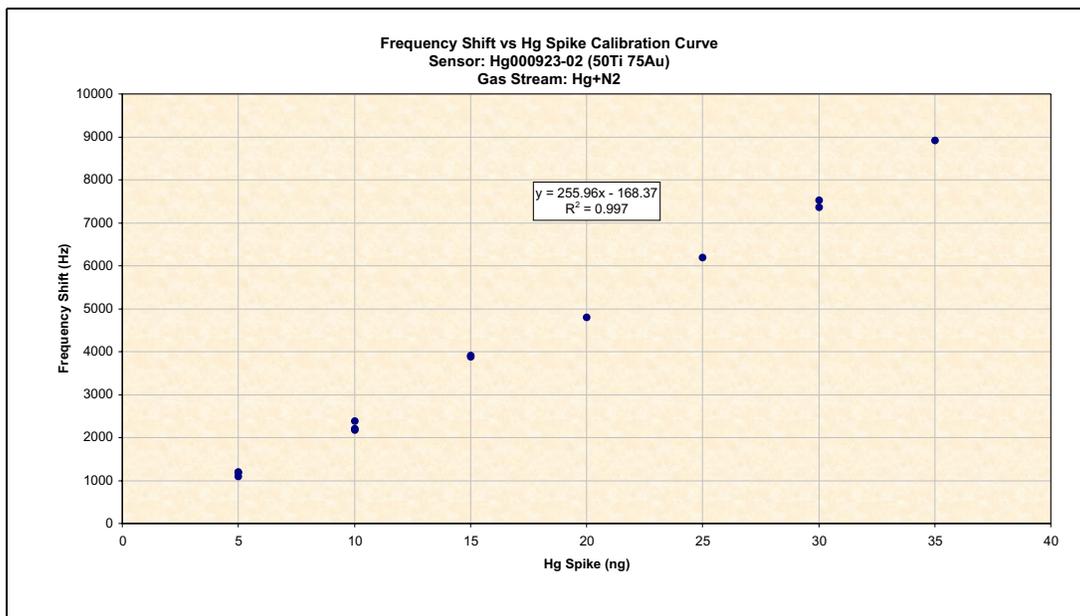


Figure 24: Saw Sensor 2 - Mercury Spike Calibration.

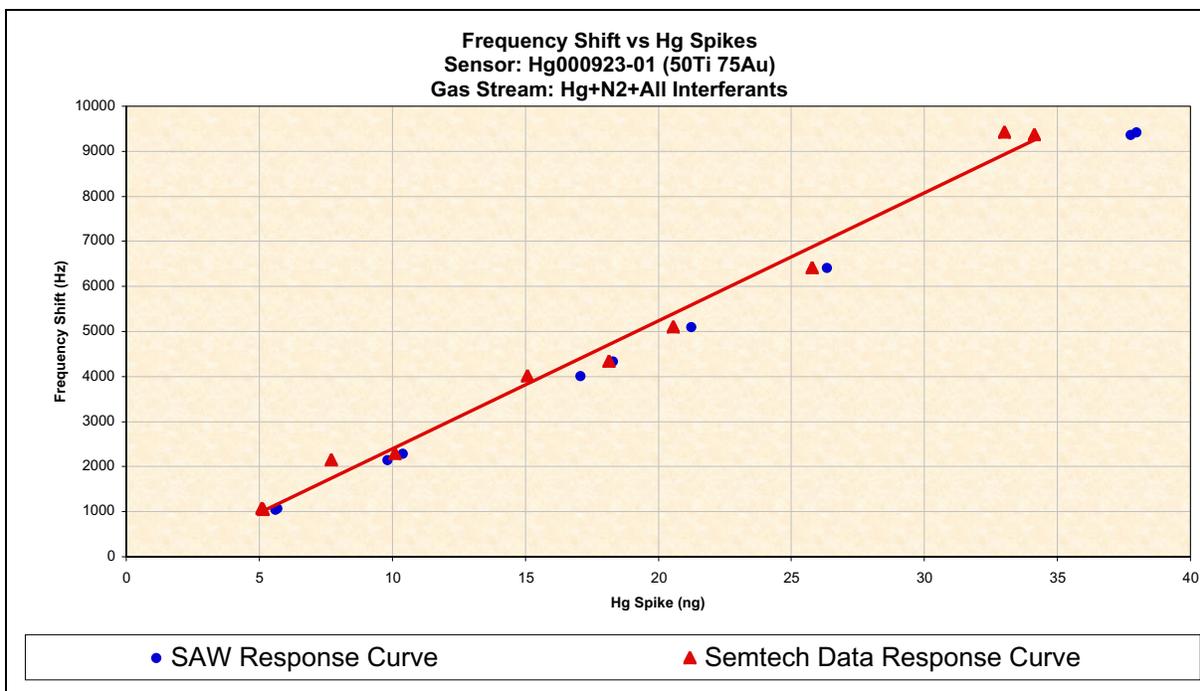


Figure 25: A comparison of SAW Sensor 1 and the Semtech AA detector.

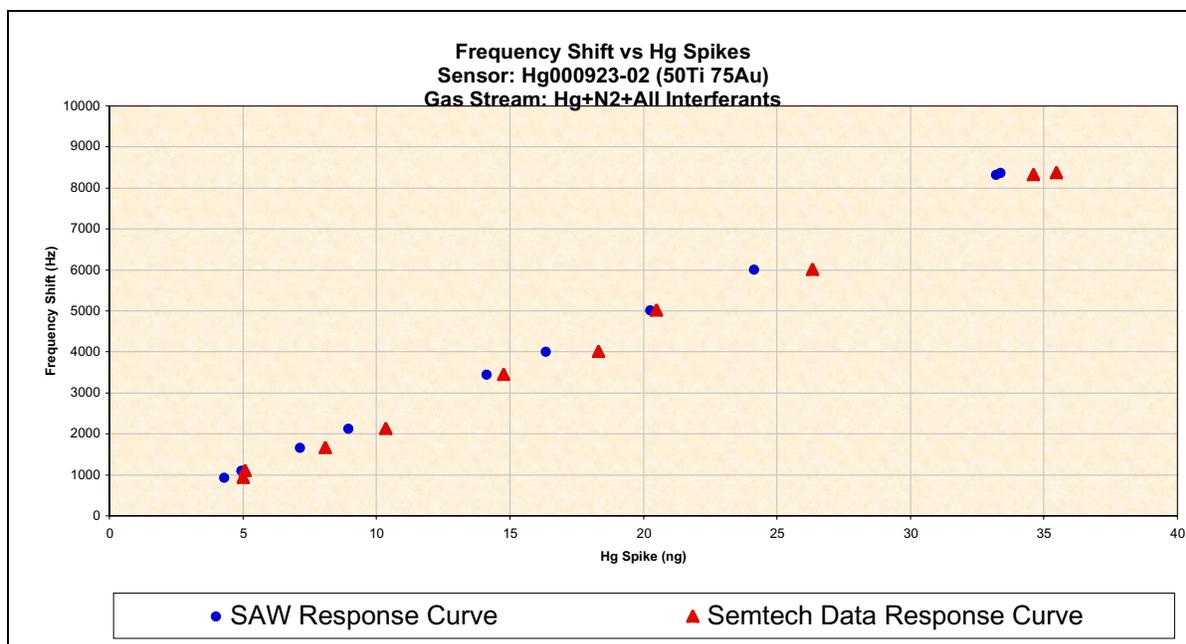


Figure 26: A comparison of SAW Sensor 2 and the Semtech AA detector.

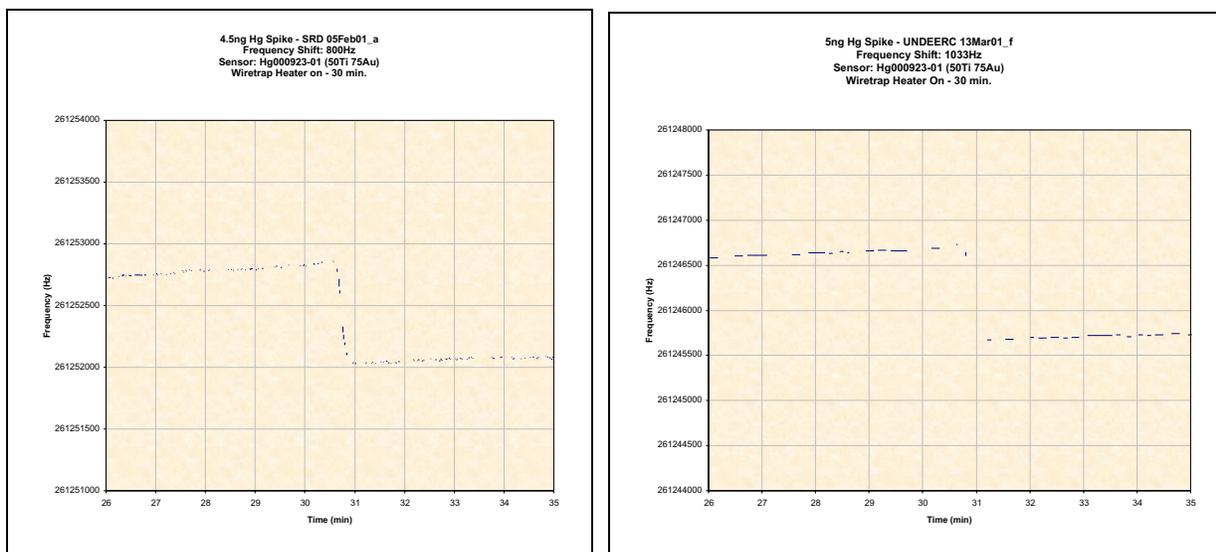


Figure 27:

a) Sensor Response @ SRD prior to the test. b) Sensor Response @ EERC during the Spike Experiments.

Continuous Test Results:

Following the completion of the spike experiments, the SAW instrument was then coupled directly to the output of the UNDEERC sampling and gas preconditioner as per Figure 13. Since there was no independent method of determining the actual output gas composition, initially exposure was limited to one sensor. The preconditioner was set to run a Hg concentration of approximately 12 $\mu\text{g/dscm}$ and with only O_2 , CO_2 , and H_2O flowing through the system. An immediate negative response was noted upon the introduction of a sample flow to the sensor. Figure 28 gives a series of the sensor responses as it was exposed initially (first 3 responses) to preconditioner output when only O_2 , CO_2 , and H_2O are introduced. The slope reduced from the approximately 3000 Hz/min measured at SRD to 250 Hz/min. A further small reduction is seen when (next 3 responses) all the interferences are introduced.

As a result of prior experience, the initial conclusion reached was that contaminants were present in the output. At this point, it was decided to expose another working sensor to the output of the preconditioner. The response of the second sensor can be seen in Figure 29. An abrupt reduction in sensor response was once again very evident. At this point, the conclusion was reached that contaminants were present in the output from the preconditioner and that it was poisoning the sensors. Various attempts were then made to restore sensor performance, but as can be seen in Figures 28 & 29, the damage appears to be permanent. This assessment was confirmed by experiments that were performed after the instruments returned to SRD. These experiments involved multiple exposure and regeneration under controlled conditions.

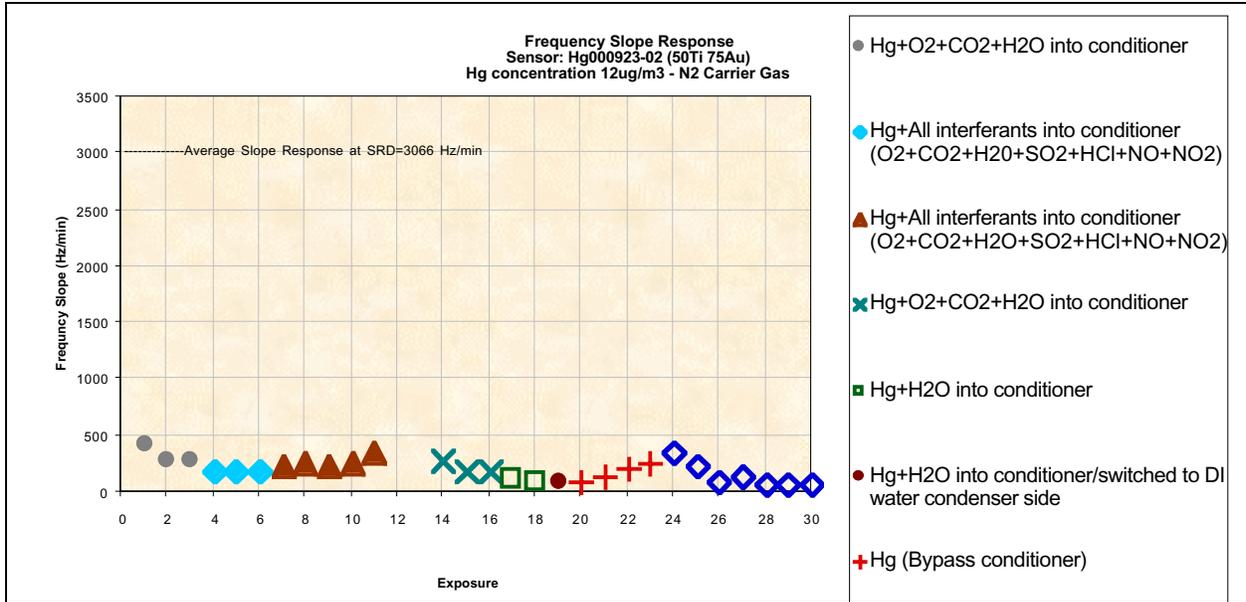


Figure 28: Frequency Response of the SAW sensor during continuous sampling of the output from the UNDEERC preconditioner.

Note: The frequency slope was nonlinear during exposures 12 & 13.

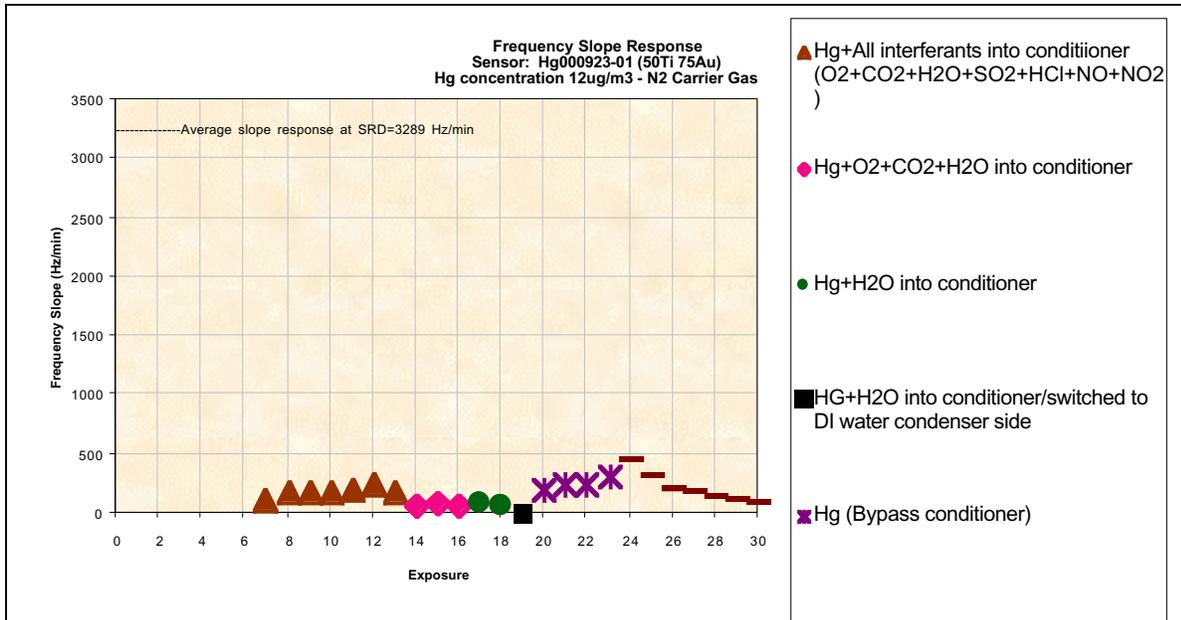


Figure 29: Frequency Response of Second SAW sensor to continuous sampling of the output from the UNDEERC preconditioner

Examples of the changes in individual sensor response can be seen in Figures 30 and 31 as the sensors were repeatedly exposed to the output from the preconditioner. In normal operation, the frequency stabilizes following sensor regeneration and there is a clear sharp response to mercury exposure. However, after exposure to the preconditioner output, the frequency shift in cooling back to 30 C is much larger, the time to stabilize is significantly longer and the response to mercury substantially impaired (see Figure 32). It was clear that this effect was due to the presence of some contaminant present in the output of the preconditioner even when no interferent gases were being introduced. While it can be conjectured that this effect was due to memory effects due to a previous breakthrough, no method was available to establish the actual components making up the output of the preconditioner. It is apparent that the sensors are impaired prior to the introduction of any acid gases into the system. In fact, it appears that the sensor response returned to a more normal response (although reduced) once the interferent gases were introduced (Figure 30). Further exposures, however, subsequently degraded the sensor response significantly. The results of the spike experiments indicate that the level of contaminates are sufficiently low as not to impact the result under those conditions. It appears that the large quantity of gold present in the gold trap (compared to a 75 μ g gold film) may play a significant role in neutralizing any contaminants before they can impact the sensor elements. This reaction indicates the need for further investigation of the role that interferents play in poisoning the sensor elements.

Figure 32 gives a more detailed picture of the changes in the behavior of sensors before and after exposure to the preconditioner output. It is very evident that something has given rise to cause significant changes in the properties of the gold films. The films have yet to be analyzed but it is expected that the results from an XPS analysis of gold will be available for the ASME review.

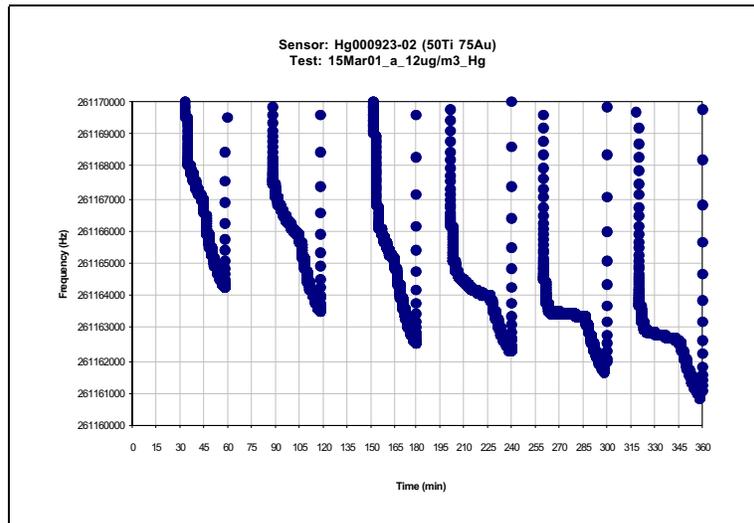


Figure 30: Sensor response to continuous sampling of the output from the UNDEERC preconditioner. First 3 responses - only O₂, CO₂, and H₂O. Second 3 responses — all interferents. Hg Concentration setting = 12 μ g/dscm (100ppbv). Total flow = 29.9 scfh (14.1 L/min).

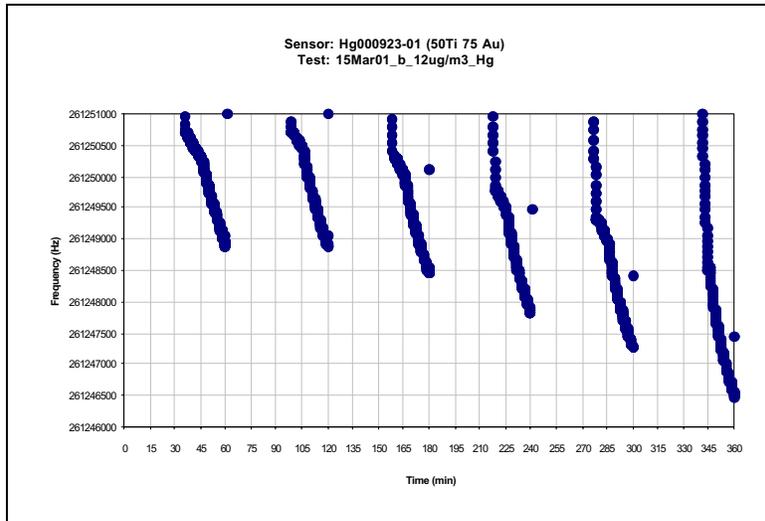


Figure 31: Evidence of the progressive deterioration of the SAW sensors with continued exposure to the output from the preconditioner.

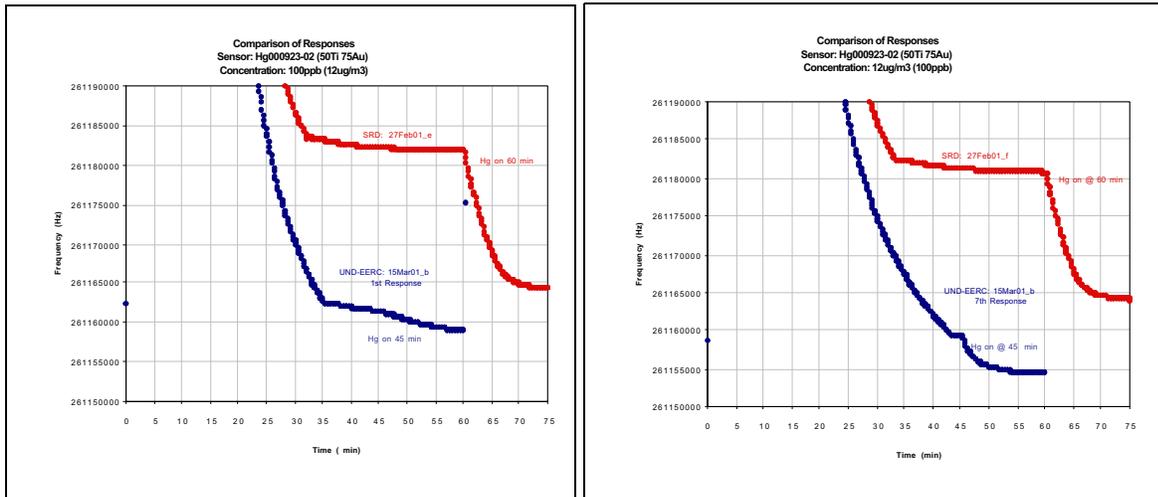


Figure 32: Comparison of sensor response before exposure to the output of the UNDEERC preconditioner with the first and seventh exposures after exposure.

Conclusions and Recommendations

The SAW sensor has consistently detected elemental Mercury concentrations under continuous sampling conditions with a detection limit of less than 1 µg/dscm in dry nitrogen. Under transient spike conditions the detection limit is larger but still less than 10 µg/dscm. Under both operating regimes, results are obtained with repeatability of better than 5% over exposure times of many hours. These results compared very well to a Statement of Work requirement of detection of less than 25 µg/dscm. The laboratory experiments have clearly demonstrated the sensitivity and repeatability of the technique.

Results to date indicate that the instrument performance exceeds contract specifications for response to elemental mercury and can operate in the presence of some common stack gases (Oxygen, Carbon Dioxide, low levels of SO₂, Organics, Water Vapor). High concentrations of acid gases such as Hydrogen Chloride were shown in the early phase of this project to have a severe negative effect on sensor response.

DOE requested that SRD circumvent this problem by using the sampling and gas preconditioning system in use at UNDEERC. A field test of the Hg SAW monitor using this preconditioner was performed in March 2001. Results obtained using gold traps to collect the elemental Hg from the output of the preconditioner confirmed the laboratory results obtained at SRD and were in very good agreement with the SEMTECH Hg 2000 AA measurements. However, the direct sampling of the UNDEERC preconditioner demonstrated the typical response of the impact of interferents on the sensors. Although the gas stream was sufficiently clean to allow the use of transient (spike) measurement, it was not clean enough for the SAW sensors to survive direct continuous contact even for a short period. No real-time data was available as to the composition of the output gas. The conclusion of this test is clear that further testing is necessary to quantify the level of interferents which impair sensor response, and to compare those levels with the available filtration technology.

The SRD sensor system has met all the SOW contractual requirements. It is recognized that a practical CEM requires additional development. SRD has identified the additional work necessary to increase both the sensitivity and selectivity of the basic sensor element, and complete the development of a complete mercury CEM capable of addressing both mixed waste applications and potentially coal burning applications. These activities have been proposed to DOE in follow-up work under this contract.

The scope of a follow-on development effort would contain work in three (3) main areas:

- 1) sensor poisoning studies - quantify the exact nature of the poisoning mechanism and design this 'weakness' into a robust system.
- 2) prototype configuration and optimization - work out the exact configuration details of multiple SAW elements to provide low- and high-concentration measurement ranges and continuous operation during SAW regeneration, as well as maximization of instrument sensitivity.
- 3) field-ready prototype packaging - UNDEERC's sample and preconditioning system is not applicable to a stack environment, as it is a "wet" system that is very large and requires a lot of attention. SRD will develop a front-end system that will meet the system requirements for a CEM.

Publications, Patents, and Theses

R. B. Haskell, A Surface Acoustic Wave Mercury Vapor Sensor. MS (Electrical Engineering) Thesis. University of Maine (2001).

R. B. Haskell, J. J. Caron. Temperature Compensated Surface-Launched Acoustic Wave Sensor. Patent Application No: 09/520,509 (filed 3/8/00).

J. J. Caron, R. B. Haskell, C. J. Freeman, and J. F. Vetelino. Surface Acoustic Wave Mercury Vapor Sensors Patent #5,992,215 (1999).

R. B. Haskell, J. J. Caron, M. A. Duplisea, J. J. Oullette, and J. F. Vetelino Effects of Film Thickness on Sensitivity of SAW Mercury Sensors *IEEE Ultrasonics Symposium*, 429 (1999).

J. J. Caron, R. B. Haskell, P. Benoit, and J. F. Vetelino. Effects of Film Thickness on Sensitivity of SAW Mercury Sensors *IEEE Trans. On Ultrason., Ferroelect., and Freq. Contr.* 45, 1393 (1998).

References

1. T. B. Brown, D. N. Smith, R. A. Hargis, Jr., and W. J. O'Dowd. "Mercury Measurement and its Control: What we know, Have Learned, and Need to Further Investigate." *J. Air & Waste Manage. Assoc* 1-92, June (1999).
2. N. B. French, S. J. Priebe, and W. J. Hass, Jr. "State-of-the-Art Mercury CEMs." *Anal. Chem., News & Features* 471A, July 1, (1999).
3. J.J. McNermy, P.R. Buseck and R.C. Hanson, "Mercury Detection by Means of Thin Gold Film", *Science*, 178, 611, 1972.
4. Jerome Division of Arizona Instruments, Product Literature.
5. E.g. Perkin-Elmer MERCCEM (www.aldora-cems.com), Verewa HM-1400 (www.durag.com), Semtech Hg 2000.
6. G. P Miller, "Development & Evaluation of an Air-Inductively Coupled Plasmas as a Continuous Emission Monitor. Vol 1. Task 1.3" Annual Report DOE Grant DE-F602-93CH-10575. April 2000.
7. D. P. Baldwin, D. S. Zamzow, D. E. Eckels, and G. P. Miller, "A Continuous Sampling air-ICP for Metals Emission Monitoring." *Proc. Of SPIE* 3853 (1999).
8. D. P. Baldwin, D. S. Zamzow and G. P. Miller, "AOTF-Echelle spectrometer for air-ICPAES continuous emission monitoring of heavy metals and actinides." *Proc. Of SPIE* 3534, 59 (1998).
9. D. P. Baldwin, S. J. Bajic, D. S. Zamzow, D. E. Eckels, S. Tao, C. A. Waggoner and G. P. Miller, "Testing of Continuous Sampling Air-ICP and Mercury Systems as Continuous Emission Monitors at the Diagnostic Instrumentation & Analysis

- Laboratory.” September 18-26, 2000. Ames Laboratory-USDOE Report IS-5144 (2001).
10. Thermo Jarrell Ash Trace Air ICP-AES system (www.thermoelemental.com).
 11. Yueh, F.Y., Singh, J.P., and Zhang, H., 2000, "Elemental Analysis with Laser-induced Breakdown Spectroscopy (LIBS)", Invited chapter in *Encyclopedia of Analytical Chemistry: Instrumentation and Applications*, Ed-in-Chief Dr. Robert A. Meyers. John Wiley & Sons Ltd. (2000).
 12. S. Tao, F. J. Mazzotti, C. B. Winstead, and G. P. Miller, "Determination of elemental mercury by cavity ringdown spectrometry" *Analyst* 125, 1021 (2000).
 13. G. P. Miller and C. B. Winstead, *Cavity Ringdown Laser Absorption Spectroscopy*, pp10734-10750, *Encyclopedia of Analytical Chemistry: Instrumentation and Applications*. Ed-in-Chief Dr. Robert A. Meyers. John Wiley & Sons Ltd. (2000).
 14. Q. Bristow "An Evaluation of the Quartz Crystal Microbalance as a Mercury Vapor Sensor for Soil Gases", *J. Geochem. Expl.*, 55, 1972.
 15. E.P. Scheide and J.K. Taylor, "Piezoelectric Sensor for Mercury in Air", *Environmental Science and Technology*, 8, 1097, 1974.
 16. E.P. Scheide and J.K. Taylor, "A Piezoelectric Crystal Dosimeter for Monitoring Mercury Vapor in Industrial Atmospheres", *Am. Ind. Hygiene Ass. Journal*, Dec. 1975.
 17. E.P. Scheide and R.B.J. Warner, "A Piezoelectric Crystal Mercury Monitor", *ibid*, 745, Sept., 1978.
 18. M.H.H., G.G. Guilbault and E.P. Scheide, "Determination of Nanogram Quantities of Mercury in Water with a Gold-Plated Piezoelectric Crystal Detector", *Anal. Chem. Act.*, 130, 141, 1981.
 19. A.N. Mogilevski, A.D. Mayorov, N.S. StroStroganova, D.B. Stavrovski, I.P. Galkina, L. Spassov, D. Mihailou and R. Zahariera, "Measurement of the Concentration of Mercury Vapor in Air through a Piezoresonance Method", *Sensors and Actuators A* 28, 35, 1991.
 20. L. Spassov, D.Y. Yankov, A.N. Mogilevski and A.D. Mayorov, "Piezoelectric sorption Sensor for Mercury Vapors in Air Using a Quartz Resonator", *Rev. Sci. Instru.* 64, 225, 1993.
 21. C. L. Britton, Jr., R. J. Warmack, S. F. Smith, P. I. Oden, G. M. Brown, W. L. Bryan, L.G. Clonts, M. G. Duncan, M. S. Emery, M. N. Ericson, Z. Hu, R. L. Jones, M. R. Moore, J. A. Moore, J. M. Rochelle, T. D. Threath, T. Thundat, G. W. Turner, A. L. Wintenberg. "MEMS sensors and Wireless telemetry for distributed systems" *SPIE 5th Inter. Symp. Smart Mat. & Struct.* (1998).
 22. R.M. White and F.W. Voltmer, *Appl. Phys. Lett.* 7, 314 (1965).
 23. T.M. Reeder, D.E. Cullen and M. Gilden, 1975 *IEEE Ultrasonics Symp.*, pp. 264-268.
 24. D. Hauden, G. Jaillet and R. Coquerel, 1981 *IEEE Ultrasonics Symp.*, pp. 148-151.
 25. M. Nakazawa, H. Ito, A. Usui, A. Ballato and T. Lukasjek, 1982 *IEEE Ultrasonics Symp.*, pp. 290-296.
 26. S.G. Joshi, 1982 *Ultrasonics Symp.*, pp. 317-320.
 27. R. Inaba, Y. Kasahara and K. Wasa, 1982 *IEEE Ultrasonics Symp.*, pp. 312-316.
 28. E. Gatti, A. Palma and E. Verona, *Sensors and Actuators* 4, 45-50 (1983).
 29. E. Gatti, A. Palma and E. Verona, 1983 *IEEE Ultrasonics Symp.*, pp. 331-335.

30. A. Palma, L. Palmieri, G. Socino and E. Verona, 1984 IEEE Ultrasonics Symp., pp. 951-954.
31. A. Palma, L. Palmieri, G. Socino and E. Verona, Appl. Phys. Lett. 46, 25-27 (1985).
32. A. Palma, L. Palmieri, G. Socino and E. Verona, J. Appl. Phys. 58, 3265-3266 (1985).
33. L. Palmieri, G. Socino and E. Verona, Appl. Phys. Lett. 23, 1581-1582 (1986).
34. L. Palmieri, G. Socino and E. Verona, 1986 IEEE Ultrasonics Symp., pp. 1093-1096
35. H. Wohltjen and R. Dessy, Anal. Chem. 51, 1470-1475 (1979).
36. J. Groetsch and R. Dessy, J. Appl. Polymer Sci. 28, 161-178 (1983).
37. D. Ballantine and H. Wohltjen, 1988 IEEE Ultrasonics Symp., pp. 559-562.
38. D. Ballantine and H. Wohltjen, Chem. Sens. And Microinstrumentation, pp. 222-236 (1989).
39. S.J. Martin, A.J. Ricco and G.C. Frye, Proc. 1989 Solid State Sens. and Actuators, pp. 98-101.
40. S.J. Martin and A.J. Ricco, 1989 Ultrasonics Symp., pp. 621-625.
41. R. Puk, J. Weber, "Critical Review of Analytical Methods for determination of Inorganic Mercury and Methylmercury compounds", *Appl. Organometallic Chem.*, 8, 293, 1994.
42. W. L. Clevenger, B. W. Smith, and J. D. Winefordner, "Trace Determination of Mercury: A Review" *Crit. Rev. Anal. Chem.* 27, 1 (1997).
43. D. B. Aeschliman and G. A. Norton. "Collection and Thermal Evolution Behaviors of Different Mercury Species Captured with Gold" *Environ. Sci. Technol* > 33, 2278 (1999).

List of Acronyms and Abbreviations

AA	Atomic Absorption
Au	Gold
AGC	Automatic Gain Control
CEM	Continuous emissions monitor
cm ³ /mi	Cubic centimeters per minute
CDMA	Code Division Multiple Access
Cr	Chromium
CVAFS	Cold Vapor Atomic Fluorescence Spectrophotometry
DOE	Department of Energy
DUT	Device Under Test
EERC	Energy and Environmental Research Center
EM	Environmental Management
FT	Fall Time
FFT	Fast Fourier Transform
GPIB	General Purpose Interface Bus
HCl	Hydrogen Chloride
Hg	Mercury
Hg ⁰	Elemental mercury
Hg(II)	Divalent mercury

HgCl ₂	Mercuric Chloride
Hz	Hertz
H ₂ S	Hydrogen Sulfide
IDT	Interdigital Transducer
k^2	Piezoelectric Coupling Coefficient
LASST	Laboratory for Surface Science and Technology
LiNbO ₃	Lithium Niobate
LiTaO ₃	Lithium Tantalate
MDL	Minimum Detection Limit
MFC	Mass Flow Controller
MHz	Megahertz
N ₂	Nitrogen
ng/min	Nanograms per Minute
OD	Outer Diameter
NIST	National Institute of Standards and Technology
NO	Nitric Oxide
NO _x	Oxides of Nitrogen
PI	Principal Investigator
ppb	Parts per Billion
ppm	Parts per Million
ppt	Parts per Trillion
Q	Quality Factor
R	Reproducibility
RF	Radio frequency
RM	Response Magnitude
RT	Rise Time
RTD	Resistive Thermal Device
RYC	Rotated Y-Cut
SAW	Surface acoustic wave
SDL	Saturation Detection Limit
SiO ₂	Quartz
SO ₂	Sulfur Dioxide
SO _x	Oxides of Sulfur
SRD	Sensor Research and Development Corporation
STS	Short Term Stability
TTE	Triple Transit Echo
TCV	Temperature Coefficient of Velocity
TSCA	Toxic Substances Control Act
m	Micron (1x10 ⁻⁶ meters)
mg/m ³	Micrograms per cubic meter
UM	University of Maine
W	Tungsten
XCO	Crystal Controlled Oscillator